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Summary of Technical Information for Selected Volatile Organic Compound Source Categories

Engineering-Science, Inc.
Arcadia, CA

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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ABSTRACT

This document is a compilation of existing information of varying detail based on a review of the technical literature, published and unpublished EPA and state or local agency reports, and state and local air pollution control regulations concerning various sources of volatile organic compound emissions. Because of its relatively limited treatment of these sources, this document should not be accorded the status of a Control Techniques Guideline (CTG) document.

This document may, however, serve in providing basic information on the various processes and emission points and, as such, may be a starting point for a state or local agency in considering VOC control on a given industry. Agencies are cautioned not to write a RACT regulation based solely on the technical material presented.

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SECTION 1

ADHESIVES APPLICATION

SECTION 1

ADHESIVES APPLICATION

PROCESSES AND EMISSIONS

Aside from the introduction of rubber and pyroxylin cements 100 years ago, there was little advance in adhesives technology until the twentieth century.

Adhesives may be either either organic, inorganic, or hybrids. The organic materials are classified according to origin as:

(1) Natural: starch, dextrins, asphalt, animal and vegetable proteins, natural rubber, shellac.

(2) Semi-synthetic: cellulose nitrate and the other cellulosics, polyamides derived from dimer acids, castor-oil based polyurethanes. We may look to this group for many new products in the future.

(3) Synthetics:

  (a) Vinyl-type addition polymers, both resins and elastomers: polyvinyl acetate, polyvinyl alcohol, acrylics, unsaturated polyesters, butadiene/acrylonitrile, butadiene/styrene, neoprene, butyl rubber, polyisobutylene.

  (b) Polymers formed by condensation and other step-wise mechanisms: epoxies, polyurethanes, polysulfide rubbers, and the reaction products of formaldehyde with phenol, resorcinol, urea, and melamine.

Alternatively, adhesives may be categorized according to the solubility and fusibility of the final glue line:

(1) Soluble, including thermoplastic (soluble and fusible): starch and derivatives, asphalts, some proteins, cellulosics, vinyls, acrylics.

(2) Thermosetting (insoluble and infusible): phenol- and resorcinol-formaldehyde, urea- and melamineformaldehyde, epoxies, polyurethanes, natural and synthetic rubbers if vulcanized.

Table 1-1 on the following page lists various adhesives and their industrial uses.

In the context of this report, the discussion of adhesives is included because of the potential for VOC emissions from organic solventborne adhesives. Thus, further discussion will be limited to this latter class of adhesives, substitutes for them, and to control technology. For the most part the natural adhesives, particularly those derived from starch, dextrins, animal and vegetable proteins and shellac, are not directly competitive with organic solvent-borne synthetic adhesives and will not be discussed further. Natural rubber-based adhesives are organic solvent-borne and will be included in the discussion of synthetic polymer type solvent-borne adhesives. Rubber type adhesives are still used to bind paper, rubber, plastic films, leather, wood, ceramic, plastic tile, metals, etc. to each other and to other materials.

Hot-Melt Adhesives

Hot-melt adhesives are generally sought for economic reasons with regard to the application process, since it is simply or quickly applied and lends itself to mechanization. If these factors are unimportant, a solvent cement or a thermosetting-type adhesive provides more durability and greater strength.

The sequence of operations in applying hot-melt adhesives is a rapid one, hence hand application is rare.

There is a wide variety of low-molecular-weight, natural and synthetic waxes and resins suited to hot-melts when formulated. Among these are:

Coumarone-indene resins
Resin and its derivatives

TABLE 1-1

MAJOR USES OF VARIOUS ADHESIVES

Adhesive Type	Abrasives & Friction Material	Book Binding	Construction & Industrial Fabricating	Fiber Glass & Safety Glass	Furniture	Leather Prods.	Pkg.	Ply-wood	Misc. Paper Products, Gummed Paper & Cloth (excl.Pkg.)	Textiles Incl. Tire Cord
Acrylates			X							
Alkyds (incl. oil free)		X		X		X	X			
Animal glues	X	X	X		X		X		X	
Asphalt			X	X			X		X	
Blood	X								X	
Casein					X		X	X	X	
Cellulosics		X	X	X		X	X			X
Epoxies			X	X						
Gums, natural							X		X	
Isocyanates			X	X					X	X
Phenolics	X			X	X	X		X		
Polyamides			X	X						X
Polyesters			X	X	X			X		X
Resorcinol	X					X	X	X	X	X
Rubbers	X	X	X	X		X	X		X	X
Silicone			X							
Soybean					X					
Starch and Dextrin	X	X			X		X		X	X
Styrene	X								X	
Urea			X	X	X			X		X
Vinyls		X	X	X	X	X	X		X	X
Waxes							X			

Reference 1

Mineral, vegetable, and petroleum waxes
Alkyds
Terpene resins
Heat-stable phenol-formaldehyde resins

All of these waxes and resins have low strength and melt easily to low viscosity fluids. They are reinforced or toughened by blending with limited proportions of higher molecular weight polymers, in order to be converted into useful adhesives. These higher molecular weight polymers include the following:

Ethyl cellulose
Polyvinyl acetate and its derivatives
Butyl methacrylates
Polyethylene
Polystyrene and styrene copolymers
Polyisobutylene

The ideal hot-melt adhesive is solid at room temperature, capable of being stored and handled easily without blocking, and is light in color. When a heat source is applied, it melts sharply and flows freely. Also, it is stable during prolonged heating and able to withstand local overheating.

Hot-melts are available in many different forms such as: tapes or ribbons, films or thin sheets, granules, pellets in various shapes such as cylinders and cubes, block and cordlike formations.

Hot-Melt Adhesive Application

Many different methods exist for the application of hot-melt adhesives. Two common methods are doctored rolls and intaglio techniques. Individual pieces are frequently dipped.

Over the past few years, a system which uses an extruder as a melting and feeding device or heat pump has been widely used. The latest system, also widely in use, is a concept which incorporates a hot-melt adhesive in cordlike form and an applicator to melt and apply it.

There are two principal types of equipment for the application of hot-melt adhesives: melt reservoir and "progressive feed". A melt reservoir involves a quantity of adhesive melted in a pot and delivered by a metering pump from the pot to a heated nozzle. The adhesive is in the form of blocks, chips, or granules. The melting pot is subjected to a charge, then heated to a predetermined temperature under thermostatic control, and the melt is fed to a nozzle or cementing wheel by a pump. The components are immediately bonded together with pressure.

Only a minimum quantity of hot-melts must be molten at any one time with the "progressive feed" application method. This is because the adhesive is fed continuously in the form of an elongated cord. The adhesive is supplied as a flexible, grooved cylindrical cord coiled on reels. The delivery rate of the melt through the nozzle is synchronized with the rate of feed of the cord. Between the feed and delivery point, the adhesive passes around a heated melt wheel running in an eccentric groove. The melt chamber is formed by the small tubular space between the wheel and the casing. Since the internal capacity of the unit is so small, only a few grams of material are held above the melt temperature inside the applicator. Using thermostatically controlled heating elements located at carefully selected points enables the adhesive to be maintained at its maximum application temperature without overheating.

Uses of Hot-Melts[2)]

There are many diverse applications of hot-melts. As production speeds increase, economics of hot-melts will become more favorable, and new uses will certainly be found.

At present, the most common uses are the following:

1. Protective coating of paper, cloth, foil, and plastic film.
2. Lamination of the same materials.
3. Structural bonding of paper, wood, and other materials.
4. Pick-up gums and spot labeling.
5. Bonding of ceramics, cork, and metal.

6. Production of articles made from paper, foil or film webs including several forms of containers and packages.

With modern application equipment using "progressive feed", and especially with the wide range of adhesive formulations available in cord-like form, a number of varied bond properties have been made possible. Some of these are:

(1) Effective bonding of flexible package at -40°F.

(2) Oil-resistive bonds retaining strength on papers with 4 to 6 percent mineral oil.

(3) Effective bonding of lightly waxed surfaces.

(4) Strong uniform bonding and sealing of polyethylene films and coatings.

(5) Strong foil bonding.

(6) Fast, effective bonding of leathers.

Process Emissions and Emission Points from Hot-Melt Adhesives

According to a contact at Bostik Chemical, Mittleton, Massachusetts, the hot-melt adhesive application method is the most widely practiced presently, and one of the reasons for this is the absence of volatile organic compound emissions. In the future, water-base adhesives will become increasingly popular for the same reason.

The only time that organic emissions are a possible threat during hot-melt adhesive application is in the event of accidental over-heating of the material, resulting in thermal decomposition.

Solvent Adhesives

Approximately 75 percent or more of all rubber-based adhesives are used in the form of solvent cements1). Noncrystalline, amorphous-type thermoplastics can be joined to themselves by applying the appropriate solvents, solvent-polymer solutions, or monomer compositions. Polymeric adhesives are generally the most likely choice for the bonding of dissimilar plastics.

Solvent Adhesive Application

The following are methods of application commonly used for solvent cementing of similar plastics.

Brush Application - Cement is brushed onto both adherends, and the parts are joined while wet. As in all solvent cementing, it is usually preferable to jig the parts in place so that they are in intimate contact until the bond is firmly set. Last traces of high-boiling solvents will often take several days or more to completely evaporate. Therefore, the joint should not be subjected to very high stresses before the setting is completed. It is sometimes desirable to mask the areas immediately adjacent to the joint to be made, since running cement will ruin the appearance of the plastic or other material being glued.

Spraying - This method is often used when either large or numerous pieces are to be cemented. Uniform application of cement is a prime advantage of this method but masking of the plastic is usually required. Adequate ventilation is necessary for protection of personnel. Although spraying provides a rapid means of application, more cement is often used than when brush coating1).

Dipping - Surfaces to be bonded are often dipped into the cement for periods ranging from 1 second to more than 30 minutes, depending on the plastic and cement used. The surfaces to be butt-joined are immersed in the cement until softened, then removed and brought into contact.

Felt Pad - This method involves the use of a thick felt pad partially immersed in a pan of solvent. The solvent "wicks" through the felt fibers by capillary action so that the surface of the pad is constantly wet. Plastic surfaces to be joined are brought into contact with the pad until properly softened. This method is especially suitable for quick assembly where extremely strong bonds are not a prime criterion and masking is undesirable.

Hypodermic Syringes - These are sometimes used to introduce cement into small, otherwise inaccessible areas where a bonded joint is desirable1).

Process Emissions and Emission Points for Solvent-Based Adhesives

VOC emissions from solvent-based adhesives result from the evaporation of solvents in the adhesive as applied. These include aliphatic and aromatic hydrocarbons, alcohols, and ketones for the most part. As in the case of surface coatings, the solvent content of adhesives can constitute the major portion of the adhesive-solvent mixture. Emissions arise mainly at the point of application and in many cases are removed with local ventilation systems. Some of the higher boiling solvents can continue to be evaporated with after removal of the bonded products from the application area. Tables 1-2 and 1-3 present the major adhesive consumers and resulting volatile organic emissions.

Adhesives and the Shoe Industry and Associated Emissions

The footwear industry is a major user of adhesives for the permanent bonding of leather and man-made materials. The adhesives are mostly neoprene (aliphatic, aromatic hydrocarbons) or urethane (ketones such as acetone or MEK).

These glues are applied automatically (extruded or rolled) or they are brushed on by hand. In what is referred to as the "fitting" room, latex (a water-base adhesive) is used. This is one of the few water-based adhesives utilized since, according to a contact at Red Wing Shoes, the water-based glues dry very slowly and do not penetrate the leather very effectively.

Until adhesive technology advances substantially toward improved water-based glues, the shoe industry must depend on solvent-based adhesives3). In limited instances, hot-melt adhesives are used to assemble various parts of shoes9). The volatile organic compounds generated at the Red Wing Shoe manufacturing facility in Minnesota are vented to the atmosphere. They are not subjected to an afterburner since the sources of VOCs are spread out through the operation3).

TABLE 1-2

PRELIMINARY DRAFT OF INDUSTRY CLASSIFICATIONS, ESTIMATES OF ADHESIVES CONSUMED, AND SOLVENT EMISSIONS

Sector	Application	1976 Use (MM lb.)	Year	Base Vol. (MM lb.)	Percent Growth/Yr.	Source	Percent Solvent Based	1976 Solvent Based Adhesive (MM lb.)	Solids (MJS)	Solvent (MM lb.)	Solvent (MM gal.)
1. Construction	Total	355	1973	280	8.2	Predicasts					
	A. Flooring, tile, wall covering	163	1966	100	5.0 MJS	Cook	50 MJS	81.5	70	24.5	3.26
	B. All Other	192				By Difference	25 MJS	48	35	31.2	4.16
2. Industrial Assembly	A. Aircraft--Total	21	1973	15	12	Predicasts	at 5 MJS	4.2	30	2.94	0.392
	B. Auto--excl. tires	274.4	1973	190	9.2	Predicasts	25 MJS	61.85	30	43.3	5.77
3. Wood Products Industries	A. Plywood and Veneer	1884	1973	1724	3.0	Predicasts	20 MJS			94.2	12.6
	B. Particle Board	1128	1973	958	5.6	Predicasts	at 5 MJS			56.4	7.52
	C. High Pressure Laminates	239	1973	200	6.1	Predicasts	~0 MJS	--	--	--	--
	D. Furniture Assembly	92.2	1973	82	4.0	Predicasts	25 MJS	23	30	16.1	2.15
	E. Other Wood Products	372.2	1973	85	63.6	Predicasts	10 MJS	37.2	30	26.0	3.47
4. Textile Products	Total	61	1973	46	9.9	DuPont	10 MJS	6.1	30	4.27	0.57
5. Footwear	Total	45	1973	44	-0.6	DuPont	50 DuPont	22.9	30	16	2.12
6. Packaging	A. Boxboard	2628	1973	2270	5.0	Predicasts	~0 MJS	--	--	--	--
	B. Boxes	620.6	1973	524	5.8	Predicasts	~0 MJS	--	--	--	--
	C. PSA Tapes and Labels	827	1974	750	5.0 MJS	DeBell and Richardson	100	827	30	578.9	77.2
	D. Gummed Tapes and Labels	127.3	1973	310	6.5	Predicasts	10 MJS			12.7	1.69
	E. Converted Flexible Packaging Products	50.6	1976	50.6		MRI	80			40.5	5.58
	E.1. Single Web										
	E.2. Multi-web (laminates)										
	F. Other Converted Paper Products	446.2	1973	417	2.3	Predicasts	10 MJS	44.6	30	31.2	4.2
7. Other	A. Glass Insulation	285.8	1973	249	4.7	Predicasts	at 10 MJS			28.6	3.81
	B. Abrasive Products	94.5	1973	86	32	Predicasts	at 10 MJS			9.5	1.27
	C. Asbestos Products	131	1973	106	7.3	Predicasts	at 10 MJS			13	1.73
	D. Printing and Publishing	197	1973	155	8.3	Predicasts	10 MJS	19.7	30	13.8	1.84
	E. Rubber Products	76	1973	75	-0.4	Predicasts	10 MJS	67.5	30	47.25	6.3
	F. Prefabricated Metal Products	1.3	1975	1.27	5 MJS	Appliance Manufacturer	~0 MJS	--	--	--	--
	G. Tires	52	1973	45	5.4	Predicasts	at 5 MJS	--	--	2.6	0.35
	H. Other	283.3	1973	220	8.8	Predicasts	75 MJS	212.5	30	148.75	19.8
TOTAL		10,241.83						1,468.95		1,210.31	161.422

Reference 11

TABLE 1-3

SUMMARY OF MAJOR SOURCES

Application Sector	Solvent Emissions (MM gal./year)
1. Pressure Sensitive Tapes and Labels	77.2
2. Other Application Including Miscellaneous Industrial and Miscellaneous Household	19.8
3. Packaging Laminates (converted flexible packaging products -- multi-web)	5.6
4. Rubber Products	6.3
5. Auto Assembly (excluding tires)	5.8
6. Construction (excluding floor tile and wall covering)	4.2
7. Other Converted Paper Products -- die cut paper and board, sanitary paper products, writing tablets, wall paper, building materials, containers excluding corrugated and fiber, paper bags and sacks, envelopes	4.2
8. Footwear	3.3
9. Floor Tile and Wall Covering	3.3

a) These areas include all sources with emissions greater than 2.5 MM gal./year with the exception of plywood and veneer, particle board, glass insulation, and other wood products, from which emissions are chiefly ethyl alcohol and methyl alcohol.

Reference 11

At that facility, which employes between 700 to 800 people, the quantity of VOC losses amounts to about 55 gallons per day (about 50 tons per year), a small amount of loss according to the shoe industry3) since International Shoe of Jackson, Missouri emits 2,000 tons per year of VOCs, and various footwear assembly facilities in St. Louis emit between 800 and 1,000 tons per year. These operations currently incorporate no organic abatement equipment9).

CONTROL TECHNOLOGY

The VOC emission problem from the application of adhesives is largely restricted to that from organic solvent-based adhesives. The trend in control technology for solvent adhesives is not to control the emissions from this type of adhesive, but rather to replace them with a non-polluting waterborne type adhesive which can perform all the functions of the solvent-borne adhesives4,5). Another alternative is to choose hot-melt adhesives which also maintain an excellent non-polluting reputation6).

Hot-melt adhesive application is the most widely used and does not incorporate control technology since this method does not result in volatile organic emissions6). Water-base adhesives will become more widely used in the future and these too do not contribute organic emissions4), hence requiring no emission control technology.

According to the South Coast Air Quality Management District (Los Angeles Basin), they know of no adhesive application operations currently using any add-on control technology. In addition, a representative from that agency reported that adhesive application operations do not pose a serious contribution to the total VOC emissions of the Los Angeles Basin. However, precipitators are recommended to abate any visible emissions due to over-heating the adhesive.

There are several advantages to using waterborne adhesives: (1) the emissions are non-polluting and satisfy the most stringent environmental requirements; (2) as the cost of petroleum rises, the cost of organic solvents will rise with it; (3) the danger of residual odor in a finished product is minimized; (4) fire hazards are eliminated, reducing insurance rates; and (5) solvent fumes that linger in the ambient air around processing machinery are absent, therefore making the workplace safer and more comfortable4).

In addition, there are the minor advantages of easy cleanup and the absence of attack on solvent-sensitive substrates.

STATUS OF REGULATORY ACTIVITIES

Currently there are no specific or local emission control regulations concerned with the application of adhesives. There are numerous general volatile organic compound emisson rules. However, the State of Virginia Air Pollution Rules exempts adhesives from the general VOC emission regulations.

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SECTION 2

ASPHALT AIR BLOWING

PROCESSES AND EMISSIONS

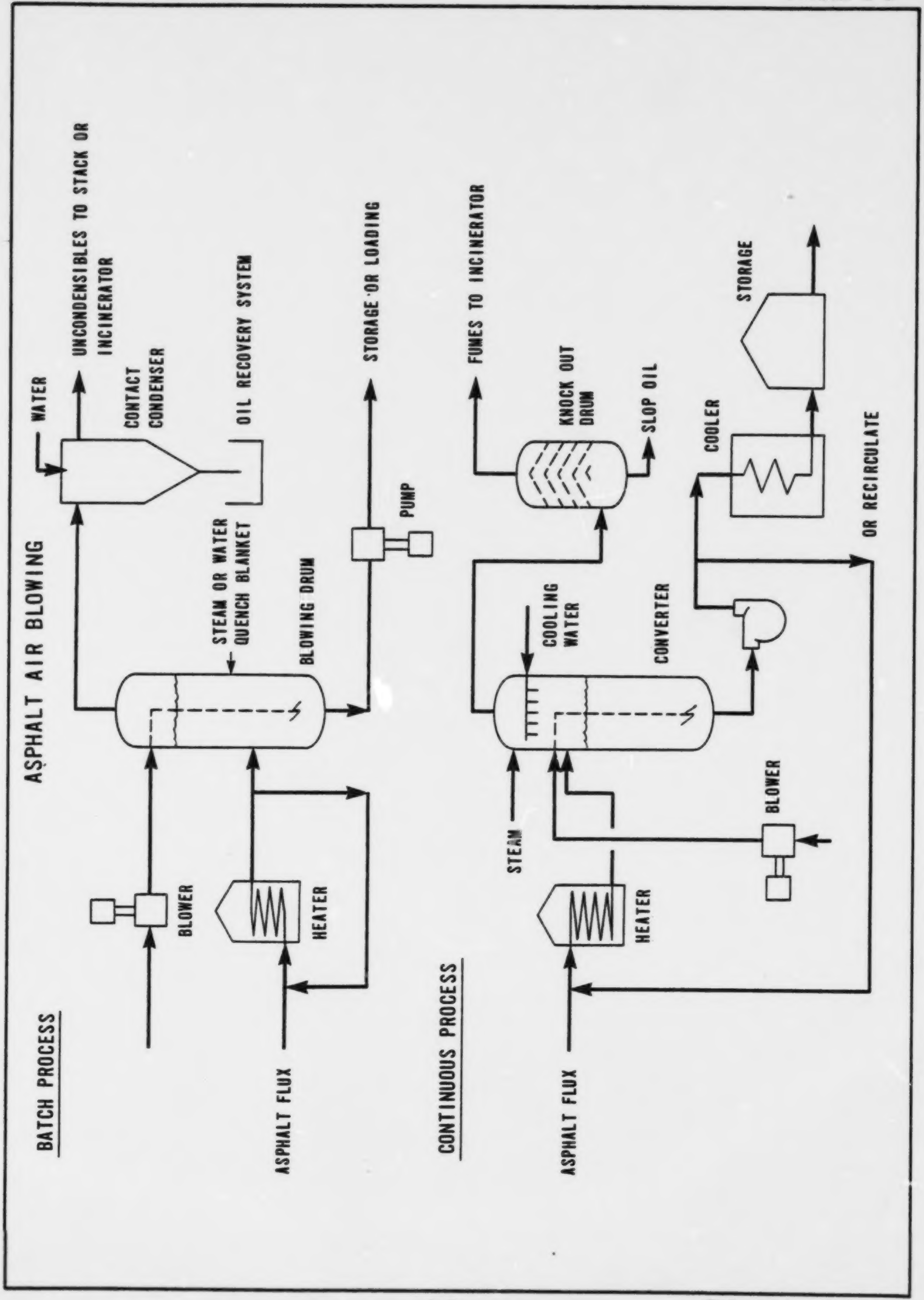
Asphalt is produced largely from residues of atmospheric or vacuum distillation of crude oil. Some is derived from propane de-asphalting. Over 99 percent of that used is from petroleum refinery sources, with ever decreasing amounts of natural asphalt from seepage being used[1]. Asphalt from these sources can be used directly or modified by air blowing. Air blowing of asphalt stock (flux) converts it to a harder product by air contact at a temperature of 200°C to 240°C (392°F to 464°F). The process is largely a dehydrogenation process with the vacated sites stimulating condensation or polymerization of the asphalt. The reaction is exothermic and water is a principal by-product. Most of the asphalt air blowing is carried out in petroleum refineries or asphalt processing plants, with the remaining amount being done in roofing plants.

Air blowing is conducted in horizontal or vertical vessels, and can be carried out batch-wise or continuously (Figure 2-1). Vertical stills are more effective because of longer air-asphalt contact time. The continuous process has advantages of better operational control, less pre-heat capacity requirement, and lower blowing losses. The continuous process usually operates at a constant temperature (260°C = 500°F) and constant liquid level.

While the largest use of asphalt is for paving (about 75 percent), relatively little paving asphalt is air blown[2]. Approximately 20 percent of asphalt production is consumed in manufacture of roofing products. Some is used as saturant in asphalt roofing felt and some is used as a coating. All roofing asphalts are air blown. About 5 percent of asphalt goes to cements, coatings, emulsions, pipe coatings, auto undercoatings, laminates, water proofings, potting compounds, and nearly 200 other uses. Some of these use air blown asphalt.

Process Emissions and Emission Points

Emissions from asphalt air blowing include both gases and aerosols. Excluding the nitrogen, residual oxygen and water of formation, most of



ASPHALT AIR BLOWING

BATCH PROCESS
ASPHALT FLUX
BLOWER
HEATER
STEAM OR WATER QUENCH BLANKET
BLOWING DRUM
WATER
CONTACT CONDENSER
UNCONDENSIBLES TO STACK OR INCINERATOR
OIL RECOVERY SYSTEM
PUMP
STORAGE OR LOADING
CONTINUOUS PROCESS
ASPHALT FLUX
HEATER
STEAM
BLOWER
COOLING WATER
CONVERTER
KNOCK OUT DRUM
FUMES TO INCINERATOR
SLOP OIL
COOLER
STORAGE
OR RECIRCULATE

the gas phase emissions are hydrocarbons. Relatively little oxygen is retained in the asphalt, but some oxygenated hydrocarbon products are formed. The lower molecular weight hydrocarbons, oxygenates, and some contaminant sulfur and nitrogen compounds are carried out of the blowing still together with nitrogen, air, and water vapor. It is conventional practice, even without specific air pollution control regulations, to pass these off-gases through a knock-out drum or condenser prior to discharge to the atmosphere vent stack. Some aerosols and condensibles are removed from the effluent stream prior to discharge to atmosphere. Relatively little testing has been performed on blowing stills*.

CONTROL TECHNOLOGY

From a practical point of view, only thermal afterburners have been used to control emissions of volatile organic carbon from asphalt air blowing. Afterburners are effective in destroying odiferous gases and will combust non-condensible VOC emissions as well.

Afterburners are classified as either thermal (i.e., direct flame) or catalytic. The primary advantage of catalytic afterburners is that they use much less supplemental fuel than an equivalent thermal afterburner. Catalytic afterburners are not used or recommended for control of hydrocarbon emissions from asphalt blowing stills because the catalyst is subject to rapid poisoning and plugging due to constituents of the fumes from asphalt processes3).

Thermal afterburners destroy combustible pollutants through oxidation to CO_2 and water. Temperatures of 650° to 760°C (1200° to 1400°F), maintained for 0.1 to 0.3 seconds of fume residence time, are sufficient to obtain nearly complete oxidation of most combustible pollutants4). Destruction of most hydrocarbons occurs rapidly at 593° to 650°C (1100°

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*Data collected by EPA shows uncontrolled gaseous hydrocarbon emissions ranging from about 6,000 to 9,000 ppm. At the plant tested this is equivalent to an average emission factor of 1.32 lb. VOC emissions per ton of saturant asphalt blown and 3.48 lbs. per ton of coating asphalt.

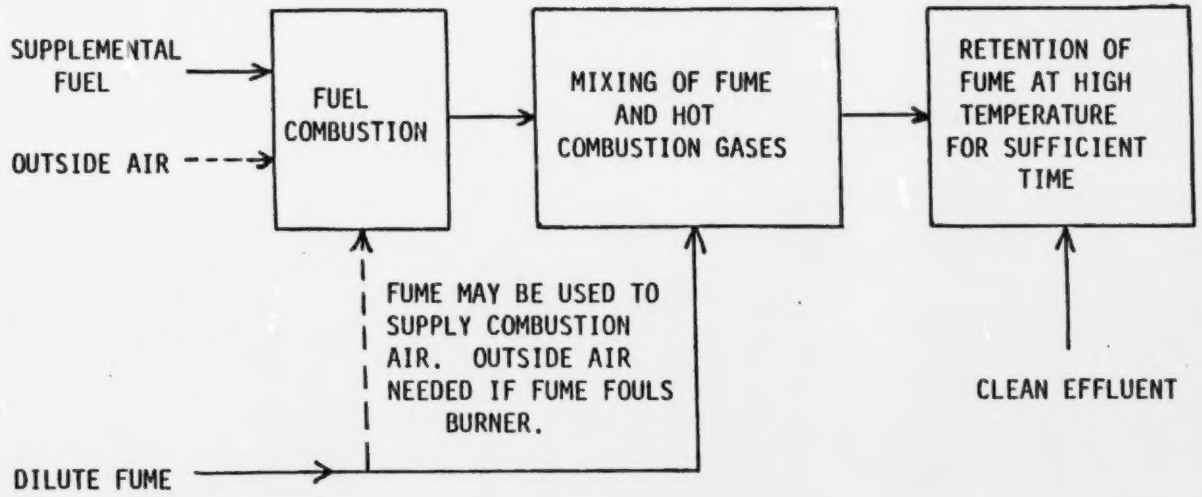
to 1200°F), but destruction of some organic compounds, such as methane, and the oxidation of CO to CO_2 requires longer residence times and higher temperatures. Temperatures of 760° to 816°C (1400° to 1500°F) may be required if the methane content of the hydrocarbon is over 1000 ppm[4]. Large droplets (50 to 100 micron) require longer residence times at the above temperatures; however, these large droplets are also easily removed in simple cyclones and knock-out vessels[4].

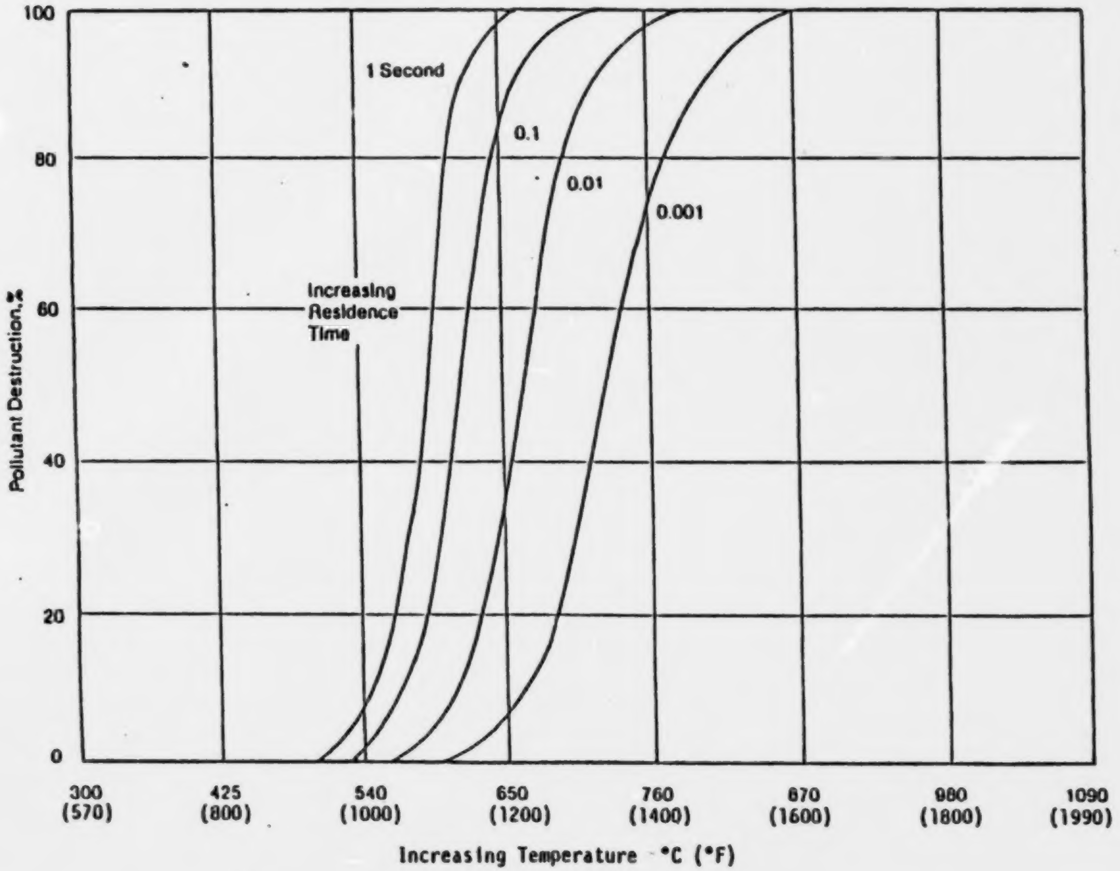
The steps involved in dilute fume incineration are shown schematically in Figure 2-2. As shown in the figure, part of the fume stream is sometimes bypassed around the fuel combustion process to preclude flame quenching and combustion instability. In the case of exhaust streams containing emissions from asphalt blowing, it is common to use only outside air in the combustion of fuel, since burner fouling is a problem. For other asphalt roofing processes, burner fouling seems to be less of a problem, and the fume stream is often used as a major source of combustion air. The fume not used for combustion must then be mixed with the hot combustion products to give a uniform temperature to all fume flowing through the afterburner. This mixing should be done as rapidly as possible without causing flame quenching so that sufficient residence time can be provided at the required temperature. Temperature and residence time are somewhat interchangeable; a higher temperature allows use of a shorter residence time and vice versa. This is illustrated in Figure 2-3 which indicated that for a 0.1 second residence time the efficiency of pollutant oxidation varies from 90 percent at 666°C (1231°F) to 100 percent at 725°C (1337°F). For a 1.0 second residence time, the efficiency varies from 90 percent at 623°C (1153°F) to 100 percent at 666°C (1231°F).

The typical effect of operating temperature on the effectiveness of thermal afterburner destruction of hydrocarbons is shown in Figure 2-4. The figure shows that the efficiency of hydrocarbon destruction varies from about 90 percent to almost 100 percent over a temperature range of about 677°C to 760°C (1250°F to 1400°F). For a given level of pollutant destruction for different afterburner designs, the major factor that influences the residence time required at a given operating temperature (above about 538°C [1000°F]) is the effectiveness with which the fume is

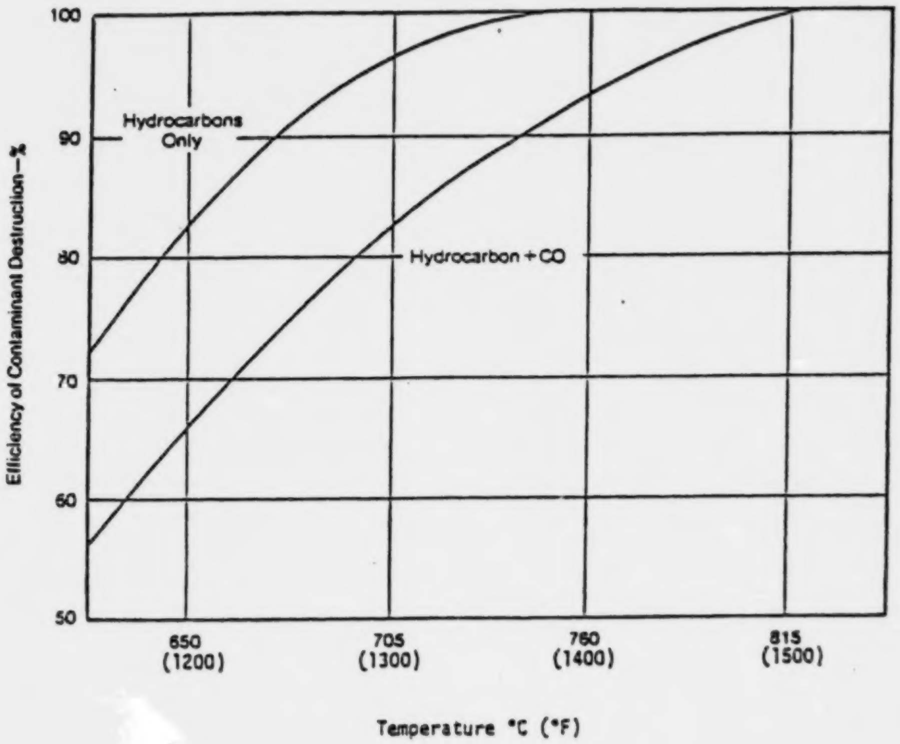
FIGURE 2-2

Steps required for successful incineration of combustible dilute fumes in a thermal afterburner:


SUPPLEMENTAL FUEL
OUTSIDE AIR
DILUTE FUME
FUEL COMBUSTION
MIXING OF FUME AND HOT COMBUSTION GASES
RETENTION OF FUME AT HIGH TEMPERATURE FOR SUFFICIENT TIME
FUME MAY BE USED TO SUPPLY COMBUSTION AIR. OUTSIDE AIR NEEDED IF FUME FOULS BURNER.
CLEAN EFFLUENT



Coupled effects of time and temperature on rate of pollutant oxidation.4)



Typical effect of operating temperature on effectiveness of thermal afterburner for destruction of hydrocarbons and carbon monoxide.4) mixed with the combustion products. If hydrocarbons are present in the exhaust gas of any afterburner operating at a nominal combustion chamber temperature above 760°C (1400°F) (or above 649°C [1200°F] for all but a few hydrocarbons), it is due to poor mixing and non-uniform treatment of the fume stream or too short residence time of the fume at temperature. Typically, afterburners are designed with average residence times which vary from 0.1 to 0.5 seconds, but the amount of time required to raise the cold fume up to the desired temperature often exceeds this average residence time. Also, not all portions of the fume are in the combustion chamber an equal amount of time; some portions are swept out very quickly while others are retained for an appreciable time. The variation in residence time, which is a function of flow patterns in the combustion chamber, can appreciably affect afterburner performance. In practice, operating personnel compensate for deficiencies in design by increasing the operating temperature of the thermal afterburners during the start-up phase until a temperature is reached which produces the desired pollutant destruction.

Little maintenance is required on most thermal afterburners. The main operating problems involve safety controls, erosion or cracking of refractory linings, heat exchanger fouling, or mechanical failure and bearing failure in the fans.

The major distinguishing feature of thermal afterburners, as compared to non-combustion control techniques for hydrocarbons, is the use of fuel. Because exhaust gases from the afterburner are typically at 649° to 816°C (1200° to 1500°F), many asphalt roofing plants use heat exchangers to recover the waste heat. This recovered waste heat may be used for many of the plant processes.

Thermal afterburners, like all combustion sources, have the potential for generating secondary pollutants due to oxidation of nitrogen, sulfur, and metals in the fume or fuel. Thermal afterburners, in comparison with power plant boilers and industrial furnaces, have low NO_x emissions because of their lower operating temperatures. The low operating temperatures and dilution of combustion products by excess air and fume results in a NO_x effluent concentration of 5 to 15 ppm. Emissions of SO_2 depend on the sulfur content of the fuel burned and on the sulfur content of the fume because almost 100 percent of this sulfur will be converted to SO_2.

Costs for controlling blowing stills in model plants have been estimated by the U.S. EPA3). In all cases the air blowing was conducted as part of operations at integrated roofing plants. Model plant asphalt production ranged from 46,200 Mg/yr. (50,931 tons/yr.) to 116,219 Mg/yr. (128,122 tons/yr.). Still sizes ranged from 75.7 m^3 (20,000 gals.) to 94.6 m^3 (25,000 gals.). The basis for control was an afterburner having a design operating temperature of 815°C (1500°F) and a residence time of 0.3 to 0.5 seconds. Depending upon the size of the plant, the cost effectiveness for particulate phase organics controlled ranged from $98/Mg ($89/ton) to $134/Mg ($121/ton). These figures cannot be used directly for the vapor phase portion of the organic emissions. Since particulate phase organic emissions from blowing stills are about six times as high as vapor phase organic emissions, the cost effectiveness on the vapor phase portion alone would be about six times as high as the figures reported above. The proper allocation of control costs, therefore, depends upon whether one or both of the two classes of organic emissions require emission controls.

STATUS OF REGULATORY ACTIVITIES

Existing air pollution control rules and regulations at the state and local level have been directed at particulate emissions, visible plumes, and odorous emissions from asphalt air blowing. While there are no regulations directly affecting volatile organic compound emissions from this source, the Bay Area Air Quality Management District in California does have a regulation covering asphalt air blowing which requires incineration of the effluent at not less than 650°C (1202°F) for a period of not less than 0.3 seconds. This rule is directed towards odors but would be effective in controlling VOC emissions as well. A copy of the rule is attached. Performance standards under consideration for the asphalt roofing manufacturing industry under Section 111 of the Clean Air Act (42 U.S.C. 7411), as amended would include asphalt blowing stills at roofing plants and refineries as affected facilities. The numerical performance standards under consideration are based upon mass emission rate of particulates and upon opacity. VOC emissions are not directly affected. However, afterburners are the only demonstrated means of control for blowing still emissions. Tests conducted on a well designed afterburner indicate that VOC emissions, as well as organic particulates are reduced by the use of afterburners. VOC reduction efficiencies exceeded 99 percent in all tests conducted for the New Source Performance Standards study.

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REGULATION 12
MISCELLANEOUS STANDARDS OF PERFORMANCE
RULE 3
ASPHALT AIR BLOWING

12-3-100 GENERAL

12-3-101 Description: This Rule applies to operations involving the air blowing of asphalt.

12-3-300 STANDARDS

12-3-301 Processing of Gases: A person shall not engage in the air blowing of asphalt unless all gases, vapors and gas-entrained effluents are incinerated at temperatures of not less than 650°C (1202°F) for a period of not less than 0.3 seconds; or processed in a manner which is equally or more effective for the purpose of air pollution odor control as determined by the APCO.

12-3-500 MONITORING AND RECORDS

12-3-501 Monitoring: A person incinerating or processing gases, vapors or gas-entrained effluents pursuant to this Rule shall provide, install, calibrate and maintain in good working order devices for indicating temperature, pressure or other operating conditions, as specified by the APCO.

2-11

SECTION 3

BARGE AND TANKER CLEANING

PROCESSES AND EMISSIONS

Cargo tanks on tankers or barges carrying crude oil, various petroleum products or other volatile organic liquids are cleaned regularly or occasionally for one of the following purposes:

- Cleaning for removal of sludge
- Cleaning for de-ballasting
- Cleaning for shipyard entry
- Cleaning of product carriers to insure product purity

This cleaning generally is conducted during or after cargo unloading in the destination port. The cleaning for removal of sludge is essentially applicable only to crude oil carriers. In the case of sludge removal, both crude oil wash (COW) and water washing methods are used. Often both are used with the water wash following the crude oil wash. Washing for other purposes is usually done with water. When human entry is required into cargo tanks, such as for repairs to be conducted in a shipyard, tanks are gas-freed by air blowing following the tank cleaning operation.

Barges are cleaned much less frequently than tankers. This is probably because many barges are in dedicated service carrying gasoline, light fuel oils, and liquid petrochemicals, e.g. benzene.

Tank washing is, of course, associated with a good deal of splashing action. As a result of this splashing and agitation, the VOC concentration in a tank can increase after cleaning. Whether and how long this condition persists is subject to a number of other factors. These include (1) method of disposal of slops (residual VOL or VOL-water mixture) -- at the loading or unloading ports or at sea, (2) whether the cleaned tank is purged with inert gas or gas-freed with air after cleaning, (3) how effective was the cleaning in removing residual volatile organic liquid, and (4) temperature of cleaning fluid.

On November 19, 1979 the U.S. Coast Guard published regulations relating to tanker safety and oil pollution which could have an impact on tanker cleaning emissions*. Under these regulations new crude carriers larger than 20,000 DWT would be required to have COW systems and existing crude carriers larger than 40,000 DWT would be required to retrofit with either a COW system, clean ballast tanks (CBT), or segregated ballast tanks (SBT). The purpose of these regulations is to reduce operational oil pollution. COW systems reduce the potential for oil pollution by reducing the clingage that remains after cargo discharge. In the case of crude oil tankers, the U.S. Coast Guard regulation assumes that clingage amounts to 0.4 percent of the original cargo. If tank washing is carried out with water, the oil-water mixture (slops) resulting is often discharged at sea. Clingage after crude oil washing is reduced to about 1/30,000 (0.0033 percent) of the original cargo. During washing the run-down puts the semi-solid oily residue back into liquid suspension. Therefore, crude oil washing is usually done during cargo discharge.

As mentioned earlier, the crude oil washing results in higher tank concentrations of VOC after cargo discharge. Therefore, the U.S. Coast Guard is requiring that tankers with COW systems and no segregated ballast tanks (used with sea water only) have the capability to conduct vapors displaced during ballasting back to tanks that are discharging crude oil. This would be done with internal vapor balance systems. Obviously, ballasting would have to be conducted simultaneously with cargo discharge operations. This inter-tank balancing should reduce or eliminate ballasting emissions at discharge ports, but filling emissions at loading ports could increase unless onshore vapor recovery systems were available.

Barges are not ballasted. However, filling emissions of VOC could increase under some circumstances if tanks are cleaned. In a study sponsored by the API[1)], three compartments in a barge previously carrying gasoline were washed with hot (180°F) water. Two tanks were subsequently air blown. Hydrocarbon concentrations in all three tanks following the washing were higher than the saturation concentration for the reported cargo temperature and RVP. Subsequent tests made during gasoline loading showed that the emissions from all three tanks were higher than those from tanks which had previously contained diesel fuel and not cleaned prior to loading with gasoline.

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*33 CFR, Part 157 - Rules and Regulations for Protection of the Marine Environmental Relating to Tank Vessels Carrying Oil in Domestic Trade, Part D - Crude Oil Washing Systems on Tank Vessels, Part 157.132 - Cargo Tanks: Hydrocarbon Vapor Emissions.

There are no satisfactory methods for predicting emissions from tank cleaning or from operations conducted subsequent to tank cleaning. A careful analysis of the operations to be conducted should, however, enable a prediction to be made as to the general direction of the effect on emissions.

CONTROL TECHNOLOGY

Tanker and barge cleaning emissions essentially result from displacement of VOC vapor mixtures from tanks after cleaning. This displacement results from ballasting or loading cargo into tanks which have been cleaned in such a way that the significant VOC concentrations are still present at time of ballasting or loading. As discussed earlier, the U.S. Coast Guard published regulations requiring internal balancing of ballasting emissions on tankers equipped with COW systems. An alternate scheme of control would be to discharge these emissions into a shore-based vapor recovery system. Such a system would not be installed exclusively to handle emissions from cleaned tanks having high VOC concentrations, but for all loading and ballasting emissions.

Where internal balancing systems are used, the tanks receiving the displaced vapors will very likely contain higher concentrations of VOC upon return to the loading port. These high arrival concentrations could be reduced by inert gas purging or gas-freeing during the return voyage. Should the loading port be equipped with a vapor recovery system, VOC emitted during loading would be controlled regardless of concentration. There are no vapor recovery systems known to be installed at marine terminals in the United States at the present time.

In the case of barge cleaning with water, the use of hot water could be avoided. Further, the cleaning should be done just after unloading instead of immediately prior to loading.

STATUS OF REGULATORY ACTIVITIES

There are no federal, state, or local regulations specifically addressed to VOC emissions resulting from tanker or barge cargo tank cleaning. The U.S. Coast Guard regulations relating to use of COW systems (mentioned earlier) do require internal tank vapor balancing during ballasting. This has the effect of reducing ballasting emissions, but possibly increasing subsequent loading emissions.

REFERENCES

1. "8-31 Marine Emissions Study, Final Report," 8-31 Technical Advisory Committee, American Petroleum Institute, Washington, D.C., 1978.

SECTION 4

BARGE AND TANKER LOADING OF VOLATILE ORGANIC LIQUIDS

PROCESSES AND EMISSIONS

The operations covered in this source category are conducted at marine terminals. These are usually located adjacent to refineries or chemical plants, but may also be operated as the terminus of a dedicated or jointly used pipeline. They may be located in deep water ports or inland waterways. Operations conducted include the loading and unloading of crude oil, gasoline, and other volatile organic liquids such as benzene. In the United States crude oil loading is rather uncommon; essentially all the crude oil arrives for unloading in tankers.

The transfer operations carried out at marine terminals have a certain degree of similarity to those conducted at conventional refinery and pipeline truck terminals and bulk plants. The major differences relate to scale of operations and the necessity to load ballast water to some vessels which would otherwise depart empty after cargo unloading. Ballasting is essentially restricted to tankers and may be done using dedicated ballast tanks or cargo tanks. Most ballasting is done in crude oil tankers. Because tanker and barge operations are rather different, they will be discussed separately. In the case of tankers we will concentrate on crude ballasting, and for barges on gasoline loading.

Crude Ballasting in Tankers

Following the discharge of crude oil cargo, sufficient ballast water must be loaded on tankers to permit them to depart port safely. Increasing numbers of tankers have sufficient segregated ballast tanks so that ballast need not be added in port to cargo tanks which contained crude oil prior to unloading. However, most of the tankers currently in service require some ballasting in cargo tanks. A ship's captain may decide to take on more than the normal amount of ballast if he decides that sea conditions require additional ballast. In such cases, it is possible that some ballasting in cargo tanks may take place even in ships with provision for segregated ballast. The amount of ballast received at the dock (exclusive of that introduced to segregated tanks) is typically about 20 percent of the crude carrying capacity of the tanker.

When ballast water is added to tanks previously containing crude oil the vapor laden atmosphere of the tank is displaced in an amount equal to the volume of ballast water added. The hydrocarbon vapor concentration is related to the vapor pressure of the crude at time of arrival, the rate of unloading, the delay after unloading prior to ballasting, whether the tank was slack (short) loaded at time of arrival, whether any lightering of cargo took place, and sun exposure of the cargo tank. Slack loading and lightering results in additional vapor space prior to dockside unloading and thus a greater opportunity for vapor concentrations to reach equilibrium with the cargo as compared to the situation with a full cargo compartment where evaporation must take place during the period of unloading and standing prior to ballasting. Delays in the start of ballasting provides time for additional evaporation from the cargo heel in the tank.

During the ballasting operation, current practice is to remove the ullage caps from the tank being ballasted. These caps are used for visual inspection of the tank at deck level and are normally closed. The term ullage refers to the ullage space, which in tanker terminology refers to the empty space above the liquid level in the tank. The vapor laden air in the tank is discharged to atmosphere during ballasting from the ullage openings. Testing of emissions from marine terminal operations has not been extensive in the sense that sufficient data has been obtained to develop accurate predictive approaches. Consequently it is not possible to quantify the influence of the parameters earlier mentioned.

Emission estimates given in this report are largely derived from testing performed in response to a request from EPA1). Tests were conducted on 22 different crude oil tankers ranging in size from 42 MDWT to 121 MDWT. Fourteen different crude oils with a volatility range from 0.7 psi Reid vapor pressure (RVP) to 8.6 psi RVP were involved in the testing. Testing covered locations on the East Coast, Gulf Coast, and West Coast. A range of crude oil and ambient air temperatures were encountered. Emissions ranged from 0.4 to 3.5 pounds of VOC per 1000 gals. of water ballast (to cargo tanks). The mid-range was slightly above 1.0 lb./1000 gals. The emission factors given for ballasting of tankers in AP-42[2)] are 0.6 lb./1000 gals. and 0.8 lb./1000 gals. water ballasted for tanks previously containing crude oil and gasoline, respectively.

VOC LOADING OPERATIONS

Gasoline, single component volatile organic liquids such as benzene, and crude oil are loaded at deepwater and inland ports in the United States. The amount of crude oil loaded is relatively small and is concentrated near coastal oil fields on the West and Gulf coasts not served by pipelines. In principal, the loading operations are similar to those conducted at truck and rail car loading terminals, except that the total volumes transferred per unit time are far greater at marine terminals than at truck or rail terminals. For example, the loading rate for gasoline into a 10,000 bbl. barge is typically about 2,000 gals./min. as compared to a tank truck loading rate of about 600 gals./min.

There are a significant number of parameters affecting the emission factors for ship and barge loading with VOL. These are broadly categorized into (1) vessel factors, (2) cargo factors, (3) cargo tank history, and (4) loading factors. Vessel factors are principally related to size and shape. Tank ships typically range from 35,000 to 120,000 DWT (cargo capacity 235,000 to 840,000 bbls.) and have relatively deep draft. Barges typically range from about 10,000 to 20,000 bbls. in capacity and are of shallow draft to accommodate passage in inland waterways. Thus the surface to volume ratio of a barge is greater than that of a tanker. This in turn permits a relatively greater potential for evaporation per unit volume of cargo.

The most important cargo factor is vapor pressure. The vapor pressure on loading conditions is best determined from the RVP and the bulk temperature of the product. The relationship between RVP and true vapor pressure is not as straightforward for crude as it is for pure compounds or for gasoline, making the estimation of crude oil loading losses less accurate than that for gasoline.

The arrival condition of empty tankers or barges is related to previous cargo and cleaning history. Arrival categories commonly used are as follows:

- Clean: Prior to loading, compartments were water-washed or gas-freed; or the prior cargo was non-volatile*.
- Ballasted: Ballast contained in compartments that previously held volatile cargo.
- Uncleaned: No treatment prior to loading and prior cargo was volatile.

The arrival condition is important in that loading emissions consist of both the VOC present in the tank prior to loading plus any additional VOC generated by evaporation of the VOL cargo being loaded.

Loading factors include fill method, initial turbulence, initial and bulk loading rates, and amount loaded expressed as a fraction of tank capacity. While loading factors are generally not taken into account in estimating marine loading emissions, the use of a lower initial rate of filling (reduced turbulence) and a rapid bulk filling rate (reduced time for evaporation from loaded liquid) could reduce emissions. The degree of tank filling is important because the concentration of emitted vapors increases with time during loading (particularly when loading uncleaned tanks). Near the end of loading when tanks are completely filled, the concentration may approach the equilibrium vapor pressure of the previous cargo (applicable in uncleaned tanks).

Emission factors in AP-42 for gasoline loading into tankers and barges have been revised fairly recently (1977). These factors are shown in Table 4-1[2]. Limited testing of gasoline loading into barges was conducted as part of the API study previously mentioned[1]. In one case, the barge was previously loaded with diesel fuel. During loading with motor gasoline of 8.5 psi RVP at a bulk temperature of 92°F, the average emission rate for three compartments was 2.2 lbs./1000 gals. loaded. In a second test, gasoline of 9.7 psi RVP was loaded into a barge which previously contained gasoline. Prior to loading, the tanks were washed with water at 180°F. Two tanks were air blown and one was not. Emission rates for the two washed and air blown tanks were 2.8 and 3.0 lbs./1000 gals. The rate from the washed only tank was 9.7 lbs./1000 gals. This condition most likely resulted from production of excess vapors which were not purged by air blowing after the hot water wash.

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*Emissions are normally less for clean tanks, other factors being equal. However, if a tank was cleaned with hot water just prior to loading, vapor concentrations could be higher than usual.

Emissions from crude oil loading are given by AP-42[2] as 0.7 lb./1000 gals. for tankers and 1.7 lbs./1000 gals. for barges. This assumes crude having a RVP of 5.0 psi. The API study showed a crude oil loading average emission rate of 1.0 lb./1000 gals. when loading Nigerian crude oil, with an RVP of 6.9 psi and a temperature of 68°F. Three compartments on one ship were tested.

CONTROL TECHNOLOGY

At the present time there are no VOC control systems on the marine (vessel) related activities at marine terminals*. The marine activities include tanker and barge VOL loading and tanker ballasting. Tank storage facilities on land associated with marine terminals utilize the same type of floating-roof tanks for volatile organic liquids as would be used in refinery or pipeline terminals, or tank farms.

Several studies have been conducted on the possible configuration and feasibility of marine terminal vapor recovery systems[3,4,5]. A major deterrent to date has been the uncertainty in the performance of safety devices at the scale-up in size required. Any such systems must be approved by the U.S. Coast Guard.

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*Under new U.S. Coast Guard regulations (33 CFR, Parts 154 and 164, and 46 CFR, Parts 30, 32, and 34, some tankers will be required to have Crude Oil Washing (COW) systems. Tankers so equipped will also be required to have inter-tank vapor balancing lines for use during ballasting. Ballasting will have to take place during cargo unloading.

TABLE 4-1

HYDROCARBON EMISSION FACTORS FOR GASOLINE LOADING OPERATIONS 2)

Vessel Tank Condition	Hydrocarbon Emission Factors					
	Ships		Ocean Barges		Barges	
	Range	Average	Range	Average	Range	Average
Cleaned and Vapor Free						
lb/10³ gal transferred	0 to 2.3	1.0	0 to 3	1.3	a)	1.2
kg/10³ liter transferred	0 to 0.28	0.12	0 to 0.36	0.16		0.14
Ballasted						
lb/10³ gal transferred	0.4 to 3	1.6	0.5 to 3	2.1	b)	b)
kg/10³ liter transferred	0.05 to 0.36	0.19	0.06 to 0.36	0.25		
Uncleaned - Dedicated Service						
lb/10³ gal transferred	0.4 to 4	2.4	0.5 to 5	3.3	1.4 to 9	4.0
kg/10³ liter transferred	0.05 to 0.48	0.29	0.06 to 0.60	0.40	0.17 t 1.08	0.48
Average Cargo Tank Condition						
lb/10³ gal transferred	a)	1.4	a)	a)	a)	4.0
kg/10³ liter transferred		0.17				0.48

a) These values are not available.
b) Barges are not normally ballasted.

The types of vapor recovery systems which possibly might be considered include low temperature refrigeration, compression type refrigeration systems, activated carbon adsorption, lean oil absorption, and incineration. All but the compression type refrigeration system will be discussed using the hypothetical facility configuration shown in Figure 4-1. This facility includes provision for tanker unloading (and thus ballasting) and barge loading. Vapor controls are shown only for the transfer and ballasting operations. Open floating-roof tanks are used for storage on shore. It is expected that these tanks would use double seals on the floating roofs. If this is the case, the seal factor currently shown in the standing loss equation for floating-roof tanks would give conservatively high emission estimates. New factors are under study by the API but they have not yet been officially published.

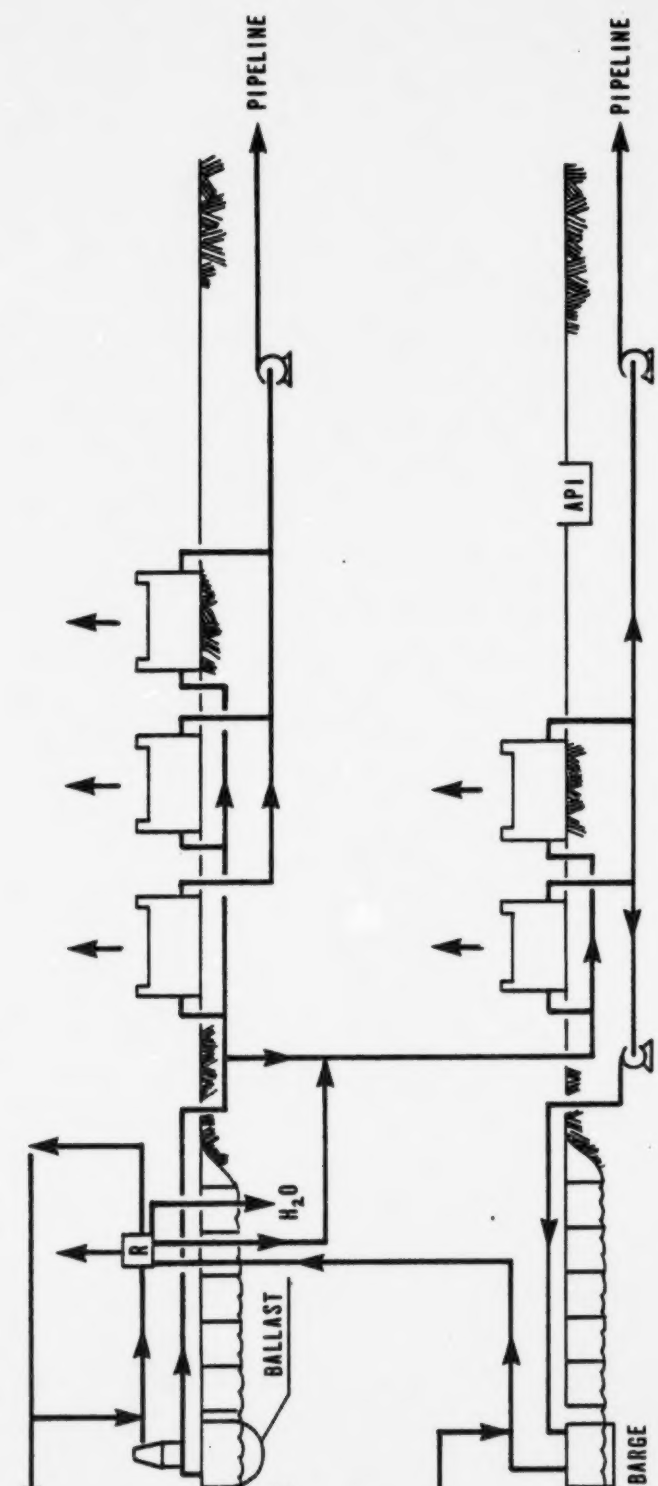
In the discussion of the possible emission control systems, no direct reference will be made to the safety issue. There is difference of opinion as to whether or not active systems designed to render the returned VOC vapor-air mixture non-flammable are necessary. Concepts involving saturation with gasoline, high ratio air dilution, blanketing with butane or fuel gas, and blanketing with inert gases (N_2 or gases from an inert gas generator). Later in this section other safety aspects will be discussed. The impact on cost will also be mentioned briefly.

Refrigeration

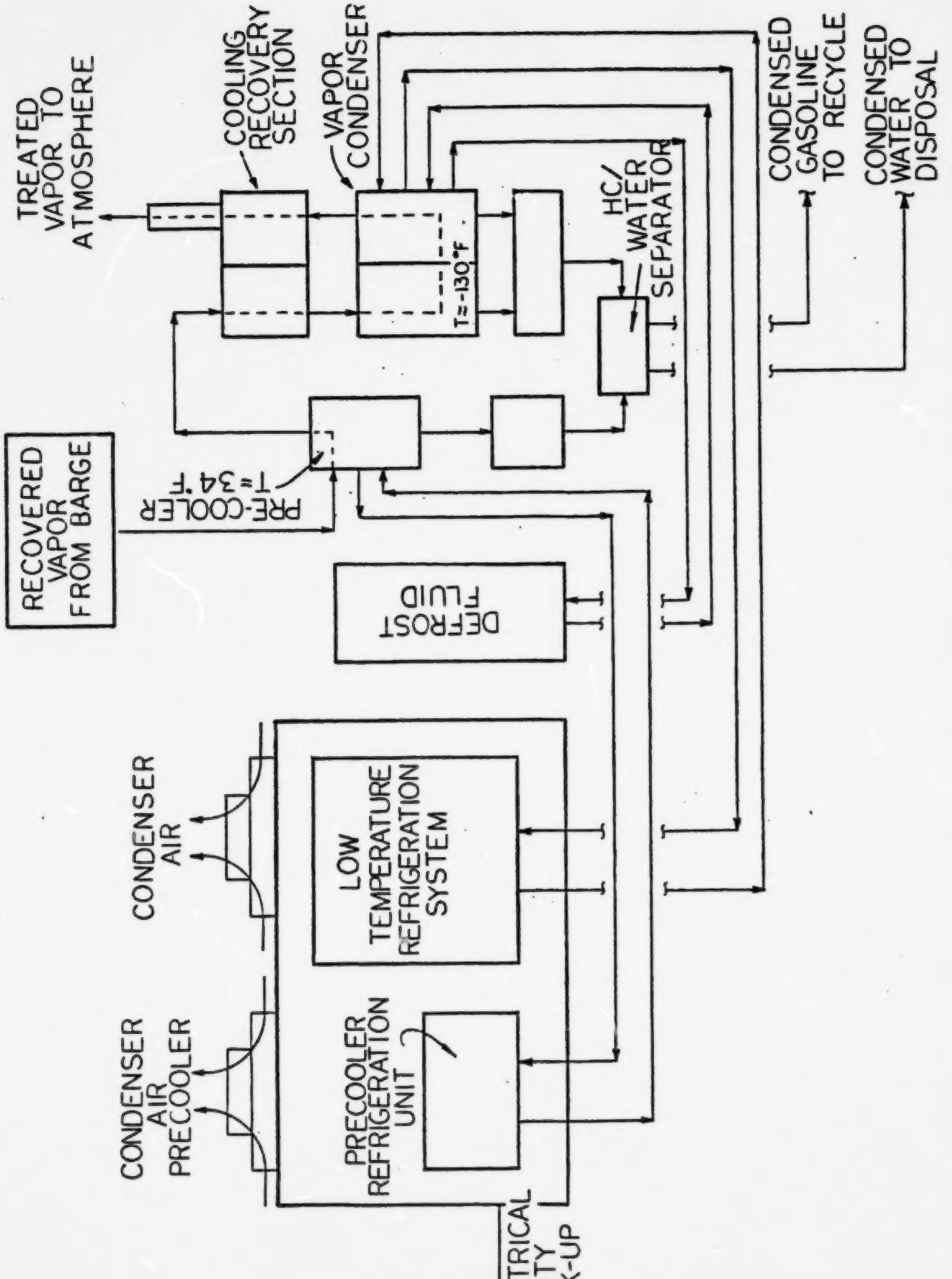
The refrigeration system discussed here utilizes two operating stages to reduce temperatures of the vapor mixture to below -100°F. The principal involves condensation of volatile organic substances at atmospheric pressure. Vapor pressures of hydrocarbons of C_3 and above are low enough at these tempertures to give high removal efficiencies. Figure 4-2 shows a schematic diagram of such a system. The system requires pre-cooling to remove water prior to passage of the vapor mixture through the low temperature sections. Water must be removed from the condensed hydrocarbons prior to the return of the recovered hydrocarbons to storage. Critical features of the system include

FIGURE 4-1

MODEL MARINE TERMINAL


TANKER
BALLAST
R
H_2O
BARGE
API
PIPELINE
PIPELINE

REFRIGERATION VAPOR RECOVERY MODULE


TREATED VAPOR TO ATMOSPHERE
COOLING RECOVERY SECTION
VAPOR CONDENSER
T=-130°F
HC/ WATER SEPARATOR
CONDENSED GASOLINE TO RECYCLE
CONDENSED WATER TO DISPOSAL
RECOVERED VAPOR FROM BARGE
PRE-COOLER
T=34°F
DEFROST FLUID
CONDENSER AIR
LOW TEMPERATURE REFRIGERATION SYSTEM
CONDENSER AIR PRECOOLER
PRECOOLER REFRIGERATION UNIT
ELECTRICAL UTILITY HOOK-UP

refrigeration module performance and correct cycling of the defrost system. The system is relatively simple, occupies little space, but is energy intensive. Hydrocarbons are recovered.

Carbon Adsorption

Carbon adsorption utilizes the affinity of activated carbon for hydrocarbon compounds to remove gasoline vapors from air. A typical carbon adsorption system consists of two or more carbon adsorber beds and a regeneration system for the carbon beds (see Figure 4-3). Two or more beds are necessary in order to keep the unit on stream during long periods of return vapor flow. This is because the adsorption bed is regenerated on batch basis. The number and size of the beds are determined by the loading of adsorbable vapors (VOC), the flow rate, the length of time required for regeneration, and the net or working capacity of the activated carbon beds. Regeneration is performed by steam or vacuum in situ.

The system illustrated in Figure 4-3 uses vacuum regeneration at a vacuum of approximately 25 mm Hg. The stripped VOC vapors (now much concentrated) are condensed or absorbed into gasoline liquid. Systems similar to the one described here have been used at gasoline truck terminals. Efficiencies of VOC control have reached as high as 99 percent.

Lean Oil Adsorption

This system uses chilled diesel oil (40°F) to absorb the VOC vapors from the air-vapor mixture. This oil which has been stripped of lower molecular weight compounds effectively absorbs butane and heavier hydrocarbons when properly designed and sized. Some portion of any propane present is also absorbed, but methane and ethane if present pass through. Following absorption of the vapors the so-called rich oil is regenerated by heating at 200°F at 150 mm Hg absolute pressure. The stripped or lean oil is cooled and returned to the storage tank.

The VOC vapors flashed off in the stripper are then usually compressed and cooled to condense the vapors and then blended into gasoline or other similar product. The lean oil absorption system is illustrated in Figure 4-4.

CARBON ADSORPTION MODULE

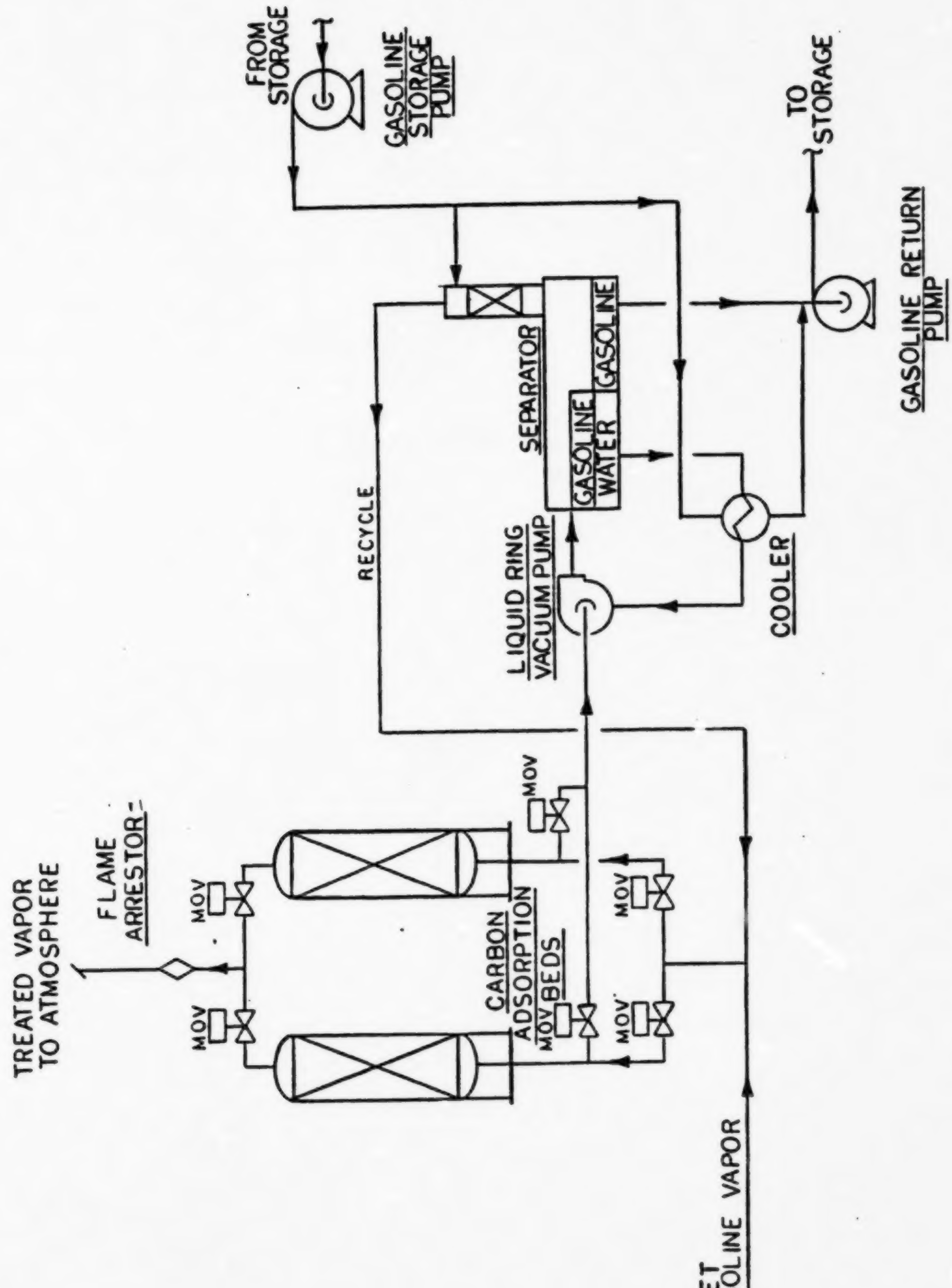
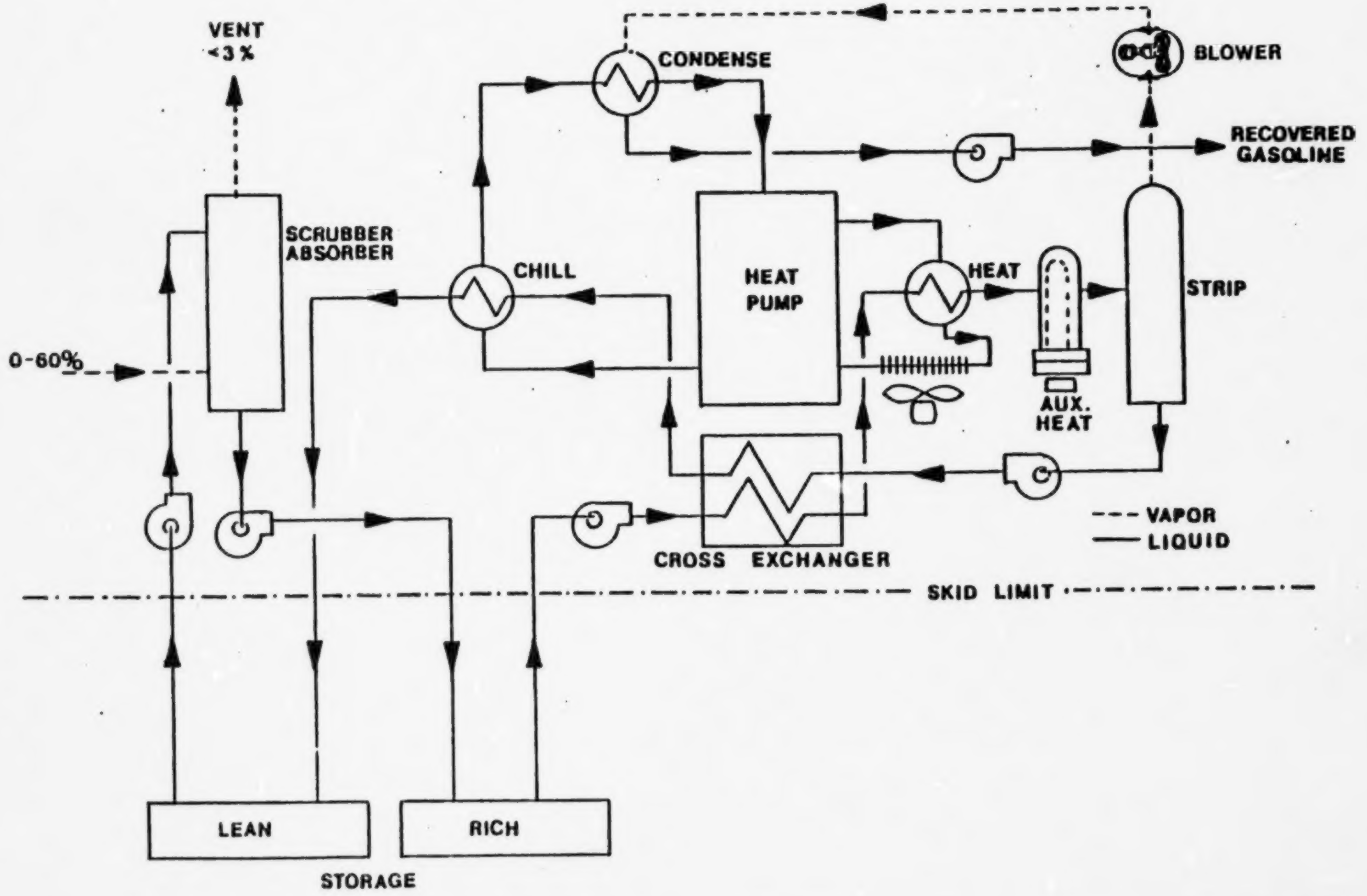

FROM STORAGE
GASOLINE STORAGE PUMP
TO STORAGE
GASOLINE RETURN PUMP
SEPARATOR
GASOLINE
WATER
GASOLINE
RECYCLE
LIQUID RING VACUUM PUMP
COOLER
MOV
MOV
MOV
MOV
MOV
MOV
FLAME ARRESTOR
TREATED VAPOR TO ATMOSPHERE
CARBON ADSORPTION BEDS
INLET GASOLINE VAPOR

FIGURE 4-4

LEAN-OIL ABSORPTION


VENT
<3%
CONDENSE
BLOWER
RECOVERED
GASOLINE
SCRUBBER
ABSORBER
CHILL
HEAT
PUMP
HEAT
STRIP
0-60%
AUX.
HEAT
--- VAPOR
— LIQUID
CROSS EXCHANGER
SKID LIMIT
LEAN
RICH
STORAGE

The effectiveness of the lean oil absorption system is dependent upon the ratio of lean oil flow to vapor flow, the purity and temperature of the lean oil, the absorption column design, and the concentration of VOC in the air-vapor mixture. One advantage of the system is the flexibility in choice of size of the absorption unit. By increasing the amount of lean oil storage, the actual processing equipment can be downsized to that required over a relatively long averaging time. Some reserve capacity must, however, be provided.

Thermal Incineration

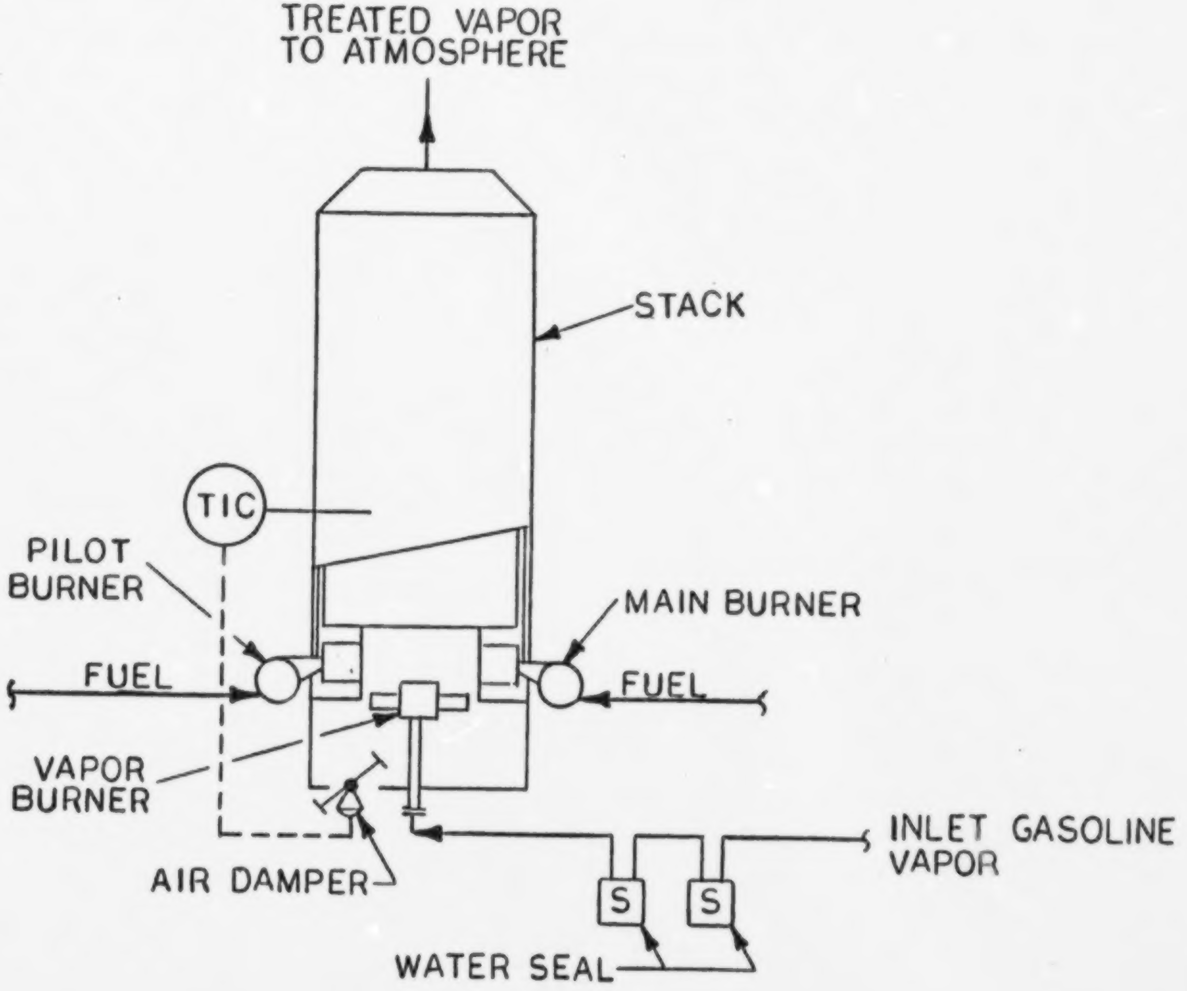
Thermal incineration (Figure 4-5) disposes of VOC by burning rather than by any of the recovery systems previously discussed. It is the simplest and most direct control system for VOC vapors available. Space requirements are relatively low. In this system the air-vapor mixture is injected into the combustion chamber of the incinerator through a burner manifold. The design combustion chamber temperature is usually about 1500°F. The residence time in the chamber is on the order of one second.

Burner and combustion chamber design must accommodate a relatively large range of flows and VOC concentrations. At the minimum this involves automatic combustion air dampers controlled by temperature. Normally, thermal incinerators have VOC removal efficiencies in excess of 99 percent. Extremely rapid changes in VOC concentration are not readily handled by the usual combustion controls, but this is not expected to be a major problem at marine terminals.

Safety Considerations

Two major safety problems are associated with marine terminal vapor control systems. These are fire (and/or explosion) and vessel over-filling. Vapor concentrations in air-vapor mixtures displaced by filling or ballasting operations are often within the flammable limits. For gasoline vapors this is 1.4 to 8.4 percent in air. Concentrations are usually lower than at truck terminals where returned vapors during filling (ballasting does not apply) are often above the upper flammable limit. Furthermore, the ultimate reservoir volume of potentially

THERMAL INCINERATOR MODULE


TREATED VAPOR
TO ATMOSPHERE
STACK
TIC
PILOT
BURNER
MAIN BURNER
FUEL
FUEL
VAPOR
BURNER
AIR DAMPER
INLET GASOLINE
VAPOR
S
S
WATER SEAL

flammable materials is much larger in the case of barges and tankers than is the case with trucks. While incorporation of vapor recovery systems at marine terminals would eliminate the discharge of vapors at deck level from open ullage caps, a new problem would be created by the connection of the onshore processing facility to the vessel. Both primary (active) and secondary (passive) safety systems can be incorporated within the design of a vapor recovery system. The primary system is designed to render the vapors emitted from the vessel non-flammable by one of three means:

(1) Dilution with air - This requires an extremely high dilution rate to reduce the vapor concentration to a safe margin below the lower flammable limit (1.4 percent) if it is assumed that the initial concentration is saturated with respect to VOC (about 50 percent in the case of gasoline).

(2) Dilution with inert gases such as N_2 or combustion gases free of CO - In this case the maximum allowable O_2 concentration is about 12 percent.

(3) Saturation - Saturation of the vapor-air mixture with butane, natural gas, or gasoline vapors will place the mixture well above the upper flammable limit.

In general, the dilution, inertion, or saturation processes described above would be designed to produce the desired results as close as possible to the point where the vapor-air mixture leaves the vessel. The primary safety modules will take up extra space and increase captial and operating costs. (Note: insurance costs with and without primary safety modules could alter this factor, assuming that any applicable safety regulations would permit construction without a primary safety module.) The secondary (passive) safety systems include all measures taken to reduce or eliminate sources of ignition, and to isolate any propagation of flame or explosion beyond barrier limits. These isolation systems incude both hydraulic and extended surface type flash arrestors.

Costs

Although no vapor recovery systems have been installed at marine terminals, similar control technology to that just described has been used at truck terminals for a number of years. Several cost estimates have been made as part of studies on application of controls to marine terminals. These studies involve differing assumptions such as the size of the terminal, activities carried out, and the volume of VOL handled on an annual basis. It is difficult, therefore, to compare the costs developed. In a study by Robert Brown Associates[3)] two different model terminals were considered. The first was a crude oil unloading terminal having berths for three 120,000 DWT tankers. Ballasting emissions only were considered. The second terminal included two berths for unloading 35,000 DWT crude oil tankers, one berth for loading gasoline to a similar tanker, and one berth for loading gasoline into a 50,000 bbl. barge. Various control scenarios were considered ranging from vapor recovery on marine operations and use of external floating-roof tanks onshore to an elaborate vapor balancing and control system interconnecting the marine operations to controlled fixed-roof storage tanks. Primary (active) safety modules were used in all cases. Capital costs ranged from $1,390,000 for the lowest cost system on the smaller combined terminal to $64,000,000 for the most expensive system on the larger tanker terminal. On a cost-effectiveness basis, annualized costs ranged from $25/ton VOC controlled to $4,000/ton VOC controlled.

Pullman-Kellog evaluated control technology and model systems for a barge terminal for loading gasoline[4)]. Two berths for 20,000 bbl. barges were used as the basis for costs. Again, primary (active safety modules were utilized in all control alternatives. Capital costs ranged from $460,000 for the lowest cost system utilizing a thermal incinerator to $902,000 for a low temperature refrigeration system. Cost-effectiveness on an annualized cost basis ranged from $240/ton VOC controlled to $480/ton VOC controlled.

MSA Research Corporation prepared an evaluation of a proposed barge loading test facility[5)]. Controls for unloading one 20,000 bbl. barge at a time were considered. No primary safety modules were included in the analysis. Capital costs ranged from $166,000 for a lean oil absorber to $292,000 for a low temperature refrigeration system. Recovered gasoline credits exceeded annualized costs in all cases. The capital recovery periods ranged from 3.7 to 18.3 years.

None of the costs given above include costs for retrofitting tankers and barges to accommodate the vapor recovery system hardware, including overflow protection. While comparisons are difficult, several factors stand out:

(1) Barge vapor recovery alone is more cost effective than tanker ballasting control because higher VOC concentrations are present in barge return vapor flow.

(2) There are some economies of scale although they are difficult to quantify at this time.

(3) Use of primary (active) safety modules increases costs (not including insurance) by a considerable amount.

(4) Costs of shore-based tank controls over and above the costs for double seal external floating-roofs results in major cost increases.

REGULATORY STATUS

There are no regulations covering emissions from marine terminal loading or ballasting operations at the federal or state level. Controls have been considered in several cases, but none have yet been installed. Control regulations will necessarily have to be coordinated with safety procedures and requirements now under consideration by the U.S. Coast Guard.

MAJOR REFERENCES

Listed References

1. "8-31 Marine Emissions Study, Final Report," American Petroleum Institute, Washington, D.C. 20037, December 1978.

2. "Compilation of Air Pollutant Emission Factors, AP-42", including supplements, U.S. EPA.

3. "Emission Control Technology for Two Model Marine Terminals handling Crude Oil and Gasoline," EPA-450/3-78-016, April 1978.

4. "Control Technology Evaluation for Gasoline Loading of Barges", EPA-600/2-79-069, March 1979.

5. Status Report by MSAR to U.S. EPA on "Demonstration of Vapor Control Technology for Gasoline Loading of Barges," Contract No. 68-02-3141, 4 December 1979.

Other

1. "API Bulletin 2514-A: Hydrocarbon Emissions from Marine Vessels Loading of Gasolines," American Petroleum Institute, Washington, D.C. 20037, 1976.

2. "Background Information on Hydrocarbon Emissions from Marine Loading Terminal Operations," Volumes I and II, EPA-450/3-76-038 a, b; U.S. EPA, RTP, NC 27711.

SECTION 5

BEER MAKING

PROCESSES AND EMISSIONS

The beer brewing process begins with malting. In this operation the barley is soaked in water in steeping tanks and transferred to germinating compartments for generally one week in order to convert the barley starch into malt sugar. Once the germinated barley is transferred to the malt drying kiln, the heat terminates the barley's growth and partly carmalizes the malt. The malt, or dried sprouted barley, is ground finely for use in the brewing operation. The mixture is heated in the mash kettle to complete the conversion of starch to malt sugar.

The mash is sent to the brew kettle after being filtered through a plate and frame filter, resulting in an extract. The spent grain filter-cake drops from the filter into the hopper and is pumped away.

The spent grain is dewatered in a screw press and dried in a steam drier. The solids are removed when the spent grain liquor from the screw press is centrifuged. The solids are marketed as cattle feed once they are mixed with the spent grain. The centrifuged liquor is returned as make-up to the rice mash-in operation.

The malt extract is boiled in the brew kettle with the hops which adds the flavor and the aroma. In the coolship, or clarifier, the insoluble proteins from the hot malt extract (called wort) coagulate and settle out. The coagulate, otherwise known as trube, is sent to a centrifuge to be separated from the wort. The recovered liquid wort is recycled into the process and the trube solids are added to the spent grain. The wort flows from the coolship to a cooler where it is cooled to fermentation temperature. During fermentation the yeast converts the malt sugar in the wort into alcohol and CO_2 gas. The beer then proceeds to the secondary fermentation tanks and undergoes the aging process where, under pressure, the beer builds-up its own natural carbonation.

After the beer has aged sufficiently, it is pumped through a series of filters for clarification. The spent filter pads are removed and processed for reuse and the beer is sent to a sterile filling room. See Figure 5-1 for a flow schematic.

There is a very low potential for ethanol emissions from beer making, but no quantitative data are readily available. Several factors mitigate against significant emissions. These include:

(1) Fermentation is conducted at relatively low temperatures, about 4.5°C (40°F) to 14.5°C (58°F).

(2) Alcohol concentration is relatively low, generally less than 6 percent by volume.

(3) Beer is kept under pressure to avoid loss of natural carbonation. It is stored at rather cold temperatures, about 0°C (32°F).

(4) Carbon dioxide released during fermentation is recovered and compressed for use in further carbonation of the beer.

Previous EPA reports suggest that there are virtually no volatile organic emissions from beer making1).

There are no known control techniques directed at VOC emissions from beer making. All known pollution control methods are directed at reducing water pollution2).

STATUS OF REGULATORY ACTIVITIES

Presently there are no known state or local regulations directed specifically at controlling VOC emissions from beer making.

REFERENCES

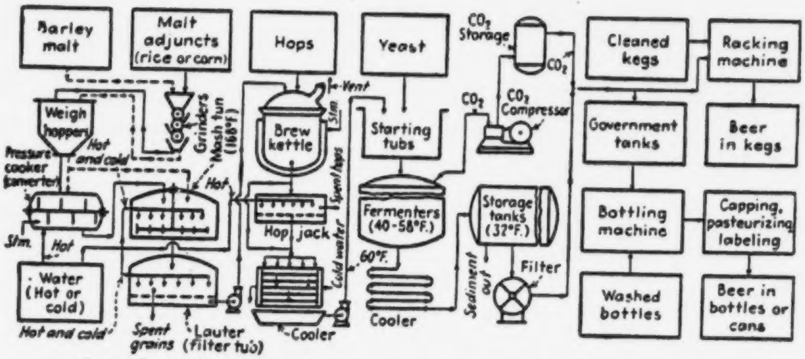
1. EPA-450/2-78-022, "Control Techniques for Volatile Organic Emissions from Stationary Source", May 1978.

2. EPA Technology Transfer, "Pollution Abatement in a Brewing Facility", prepared by U.S. Environmental Protection Agency, May 1974.

3. Shreve, Norris R., "Chemical Process Industries", Fourth Edition, McGraw Hill, 1977.

FIGURE 5-1

BEER MAKING FLOW SCHEMATIC


Barley malt
Malt adjuncts (rice or corn)
Hops
Yeast
CO2 Storage
CO2
Cleaned kegs
Racking machine
Vent
Weigh hoppers
Grinders
Mash tun (168°F.)
Brew kettle
Stm.
Starting tubs
CO2
CO2 Compressor
Government tanks
Beer in kegs
Pressure cooker (converter)
Hot and cold
Hot
Spent hops
Hop jack
Fermenters (40-58°F.)
Storage tanks (32°F.)
Bottling machine
Capping, pasteurizing, labeling
Stm.
Hot
Cold water
60°F.
Sediment out
Filter
Water (Hot or cold)
Washed bottles
Beer in bottles or cans
Hot and cold
Spent grains
Lauter (filter tub)
Cooler
Cooler

Brewer's malt	35-38 lb.	Per U.S. barrel (31 gal.) of beer.
Malt adjuncts	12-14 lb.	
Hops	½-1¼ lb.	
Yeast	¾-1 lb.	

Reference No. 3

SECTION 6

FABRIC PRINTING

PROCESSES AND EMISSIONS

This chapter discusses the four basic fabric printing operations of roller printing, rotary screen printing, flat screen continuous printing, and flat screen unit printing and the associated fabric drying and curing processes. Emissions generated from these operations and applicable emission control techniques are discussed. A review of air pollution regulations applicable to fabric printing is also presented. Fabric printing is defined as a decorative design applied to a fabric by intaglio (etched) roller, rotary screen, or flat screen printing operations.

The fabric printing industry is a subset of the textile finishing industry, which includes fabric preparation (desizing, bleaching, and mercerizing), decorative enhancement (dyeing, printing, plisseing, and felting), and functional enhancement (permanent press, softening, and soil resistance). There are approximately 200 fabric printing plants located throughout the United States, many of which perform other textile finishing operations in addition to fabric printing. A majority of the existing fabric printing plants are located in the Northeast and Mid-Atlantic regions of the country. However, the recent growth in this industry has occurred in the Southeast.

A typical fabric printing plant usually uses one type of print machine (roller, rotary screen, or flat screen). These printing operations apply a print paste in a decorative pattern onto the fabric that is passed through the printing machine. After printing, the fabric enters a drying process to remove water and organic solvents so that the fabric retains its color and pattern. Drying involves passing the printed fabric over steam cans, which are usually exposed to the ambient surroundings, or through direct-fired industrial drying ovens. Some fabrics must be further processed in a curing operation. Curing may occur in separate ovens or in a different zone within the drying oven. After the drying process, the fabric is washed and dried to remove the excess water.

Materials

This section describes the fabrics used in the fabric printing industry and the constituents of the print pastes applied to the fabrics.

Fabric

The two basic categories of fabric are knit fabric and woven fabric. Knit fabric is made by using a single continuous thread of yarn to create individual loops and to chain each individual loop to neighboring loops. Woven fabric is defined as "a fabric made by interlacing two or more systems of yarns at essentially right angles to each other."1) Woven fabric can be further divided into broadwoven fabric which is over 38 centimeters (15 inches) wide and woven terry towels. The yarns used in fabric construction are spun from either man-made or natural fibers. Man-made fibers include cellulose acetate, cellulose triacetate, nylon, polyester, polyolefin, and rayon. Natural fibers include cotton, linen, silk, and wool. The composition of these fibers determines which print pastes the fabric will accept and what texture or "hand" the fabric will have.

Print Pastes

Print pastes can be classified into the two basic categories of dispersed dye print pastes or pigment print pastes according to the coloring agent used in the print paste composition. Dispersed dye coloring agents impart color onto fabrics by becoming chemically or physically incorporated onto the individual fabric fibers. Pigment coloring agents are insoluble particles that are physically bound to fabric fibers, usually through the use of a polymerizing binder.

The other constituents of print pastes include a clear thickening agent and an aqueous or organic solvent. Thickening agents are used to facilitate the transfer of the coloring agent to the fabric during printing and to adhere the coloring agent to the fabric during drying. The desired print sharpness, yarn and fabric penetration, color value, fiber type, fabric construction, dye class, and fixation conditions dictate the selection of the proper thickening agent.2)

The remaining portion of the print paste is the solvent, which acts as the carrier for the coloring agent and the thickener.3) The solvent may be aqueous, organic, or a mixture. The organic solvent concentration in print pastes ranges from less than one percent organic solvent content by weight for dispersed dye print pastes to 0 to 60 percent organic solvent content by weight for pigment print pastes. Solvents maintain proper viscosity, aid in dye and binder dispersion, and adjust color value, sharpness of mark, and brightness of shade. Organic solvents used in the fabric printing industry are usually mineral spirits. The mineral spirits used in fabric printing operations have an average molecular weight of 155, a boiling point of 145°C (293°F), and a vapor pressure of 8.41 millimeters of mercury (0.16 pound per square inch) at 25°C (77°F).

Processes

This section describes the four fabric printing operations of roller printing, rotary screen printing, flat screen continuous printing, and flat screen unit printing and the associated fabric drying and curing processes.

Roller Printing

Roller printing is an intaglio process in which an engraved plate or roller is used to print the fabric. A print paste is applied to the engraved roller and the excess paste is removed with a doctor blade. The fabric is then placed in contact with the roller and the pressure between the roller and the central cylinder acts to transfer the print paste from the incised surface of the roller to the fabric. Figure 6-1 is a diagram of a typical roller printing machine.

Fabric, padded by a backing material or back gray, is continuously fed into the printing machine. The fabric passes between the central cylinder and a set of printing rollers. A single color print paste is applied to each printing roller which applies one portion of the pattern onto the fabric. A maximum of 14 colors can be applied to a fabric by a roller printing machine, with 8 colors being average. After printing, the fabric passes into the drying and curing processes. The cylinders

FIGURE 6-1 - ROLLER PRINT MACHINE

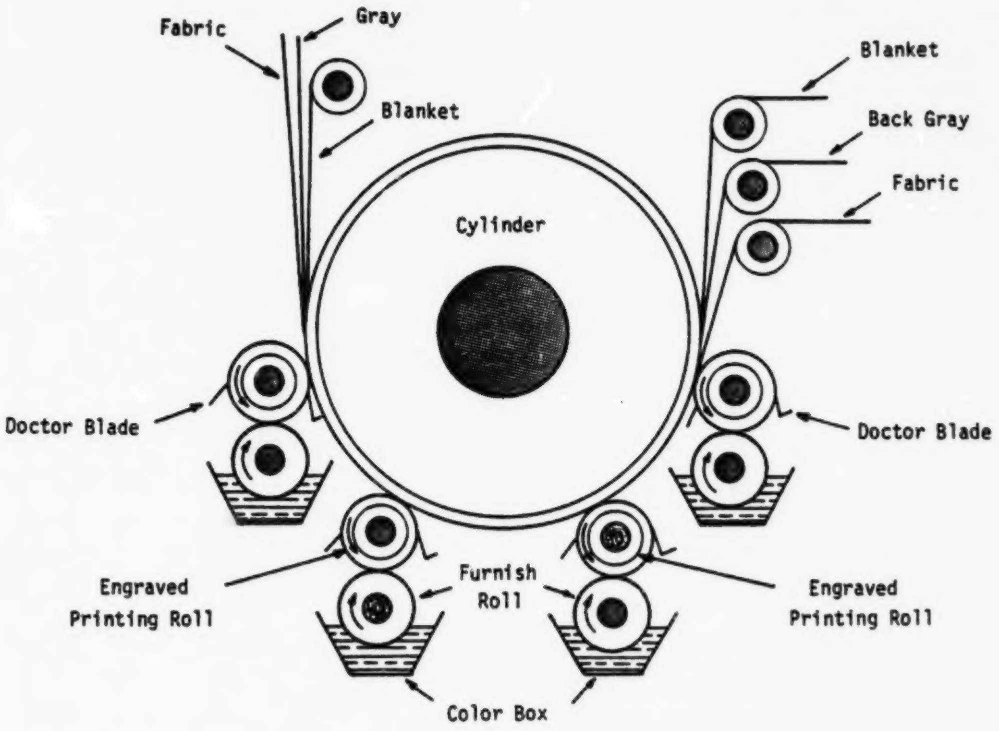
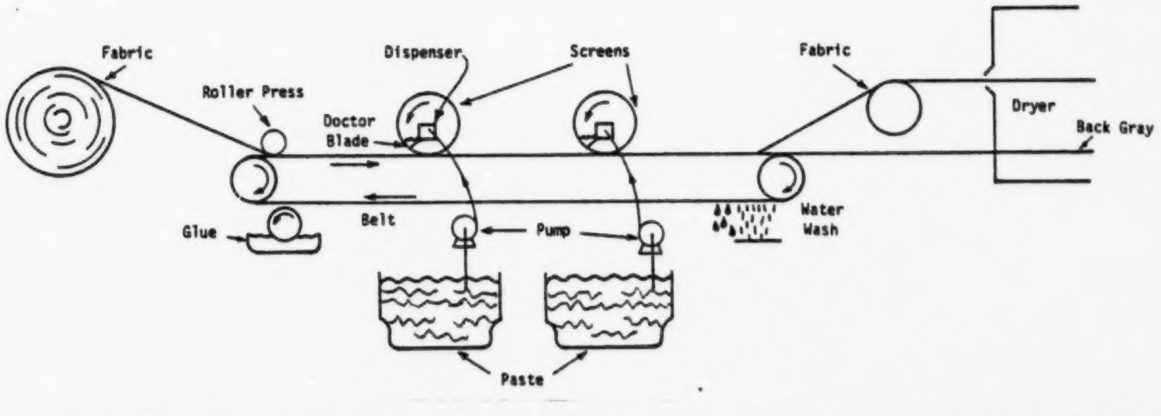

Fabric
Gray
Blanket
Blanket
Back Gray
Fabric
Cylinder
Doctor Blade
Doctor Blade
Engraved Printing Roll
Furnish Roll
Engraved Printing Roll
Color Box

FIGURE 6-2 - ROTARY SCREEN PRINT MACHINE


Fabric
Dispenser
Screens
Fabric
Roller Press
Doctor Blade
Dryer
Back Gray
Glue
Belt
Pump
Water Wash
Paste

commonly used for roller printing are copper-coated surfaces. A pattern can either be engraved or acid-etched on these copper surfaces. The engraved copper surface may be plated with chrome to create a longer lasting surface.

Several of the advantages of roller printing over rotary screen printing include sharper mark, finer line, more accurate register or fit, finer gradation of tone, smoothness of blotch prints, and better color bloom (vividness of color).4) Many of these advantages are attributable to the use of medium-to-high organic solvent content print pastes. These advantages make roller printing the preferred method for printing apparel fabrics.

Rotary Screen Printing

A typical rotary screen printing machine is shown in Figure 6-2. Fabric moves into the printing machine from left to right. The fabric is pressed between a rotary screen and a back gray as the process progresses. The fabric is attached to the back gray by a water soluble glue. Print paste is pumped from drums into a dispenser, which distributes the flow over the entire width of the application area. A stationary doctor blade forces the print paste through the screen and onto the fabric.

A screen is prepared for printing by covering it with a light sensitive chemical and then attaching a film positive of the design pattern over the screen. This sandwich is then exposed to light and an insoluble lacquer forms on the areas of the screen that are exposed to the light. The screen is then cleaned, leaving a porous screen surface in the desired design pattern. The screen is then rolled into a tubular shape. Rotary screens are commonly made of nickel or nickel alloys. Some machines are able to apply a 16 color pattern, but 12 color patterns are the maximum for most rotary screen machines.

Flat Screen Continuous Printing

Flat screen continuous printing, which is used to print drapery and sheeting on a continuous production line, is essentially the same as rotary screen printing. The two main differences between the two printing processes are the fact that rotary screens are rolled, whereas flat screens are put in a flat bed frame, and flat screen continuous printing lines operate at a slower line speed compared to similar rotary screen printing lines. The same photogrammetric method is used to prepare screens for flat screen continuous printing machines as is used for screen preparation for rotary screen printing machines.

Flat Screen Unit Printing

Flat screen unit printing is used in the printing of cut terry towels on a semicontinuous production line. In this printing process, cut terry towels are placed on a conveyor belt and moved into position under a flat screen. The flat screen is then lowered onto the terry towel and print paste is applied through the use of a squeegee that forces the print paste through the open screen areas. This process is repeated for every color in a pattern. The flat screens used for this printing process are prepared in the same manner as those used in rotary screen printing and flat screen continuous printing operations.

Dryers and Curers

After the printing process, fabrics are dried and usually cured. Drying drives off water and organic solvents so that the colors will be retained (color fixed) on the fabric. Some fabrics are color fixed during curing, which may be an entirely separate process or merely a separate segment of the drying process. Resin bonded pigment print pastes require curing. Dispersed dye print pastes may require curing but are usually color fixed during drying. Some color fixed dyes require aging in a high-heat, high-humidity environment. After the fabric passes through the drying process it is washed to remove unfixed dyes or pigments. The fabric is then dried again to remove the excess water.

Drying is accomplished through the use of industrial drying ovens (convection drying) or steam cans (conduction drying). Industrial drying ovens are heated by pressurized steam coils (indirect heat dryers) or by fossil fuel combustion (direct heat dryers). Screen printed fabrics are usually dried in industrial drying ovens because knit fabrics can be dried without tension. Fabrics requiring a soft hand, such as apparels, are usually dried by conduction on steam cans. Conduction drying is by direct contact of the fabric with the steam cans.

Industrial drying ovens have a temperature range of 149 to 177°C (300 to 350°F). The surface temperature of steam cans ranges from 93 to 135°C (200 to 275°F). Fabric residence time is 2 to 4 minutes in industrial drying ovens and 1 to 2 minutes on steam cans. Exhaust flow rates range from 18 to 600 cubic meters per minute (6,000 to 20,000 cubic feet per minute) for industrial drying ovens, and are dependent on fabric residence time, oven temperature, fabric weight, and organic solvent content and water content of the print pastes.

Curers are also heated by pressurized steam cans or fossil fuel burners. Steam can curers usually operate at atmospheric pressure under saturated steam conditions and temperatures of 163 to 191°C (325 to 375°F). Fossil fuel fired curers operate at 149 to 204°C (300 to 400°F) with exhaust flow rates of 90 to 210 cubic meters per minute (3,000 to 7,000 cubic feet per minute). Fabric residence times for curers are 2 to 4 minutes.5) Sheeting is usually dried and cured in different zones of the same oven. Decorative and apparel fabrics are usually dried and cured in separate ovens.

Emissions and Emission Sources

The sources of fugitive VOC emissions from fabric printing operations (roller printing, rotary screen printing, and flat screen continuous and unit printing) include evaporation from the wastewater stream, open print paste barrels, printing troughs, the printing rollers and screens, strike through onto the backing material or back gray, and the printed fabric prior to reaching the drying process. The steam can drying process and industrial drying ovens used to dry printed fabric are considered to be the most significant sources of VOC emissions. The steam can drying lines can be enclosed or exposed to the ambient surroundings and VOC emissions generated during steam can drying are exhausted through the use of roof vents and fans. When industrial drying ovens are used in the fabric drying process, the VOC emissions are exhausted through a stack. Most of the VOC emissions are generated during fabric drying, with only small quantities being generated during fabric curing. Figures 6-3 and 6-4 indicate sources of VOC emissions from fabric printing operations.

Operating parameters for two model printing lines are summarized in Table 6-1. These parameters are based on data obtained from fabric printing companies.6,7) Model printing line one (MPL 1) uses print pastes with a weighted average organic solvent content of 30 percent by weight and an associated drying exhaust flow rate of 255 standard cubic meters (8,500 standard cubic feet) per minute. Model printing line two (MPL 2) uses print pastes with a weighted average organic solvent content of 5 percent by weight and an associated drying exhaust flow rate of 240 standard cubic meters (8,000 standard cubic feet) per minute.

CONTROL TECHNOLOGY

The methods available for the control of VOC emissions from fabric printing operations can be classified as process modification or add-on VOC emission control systems. Process modification consists of reduction in the amount of organic solvent in the print paste composition (print paste reformulation). Add-on VOC emission control systems are primarily thermal incineration.

Print Paste Reformulation

There is little or no cost associated with the reformulation of the print pastes to reduce their organic solvent content.8) In fact there is a credit for the reduction in organic solvent usage achieved. As a result, most fabric printing operations have switched from higher organic solvent content print pastes to low organic solvent content (10 percent by weight or less) or all aqueous print pastes.9,10,11,12,13) The major reason for this changeover is the increasing cost of the organic solvents used in fabric printing. These solvents have increased in price from about $0.08 per liter ($0.31 per gallon) in 1973 to a current price of about $0.37 per liter ($1.39 per gallon).

FIGURE 6-3 and 6-4

FIGURE 6-3 - ROLLER PRINTING LINE AND ASSOCIATED STEAM CAN DRYING PROCESS

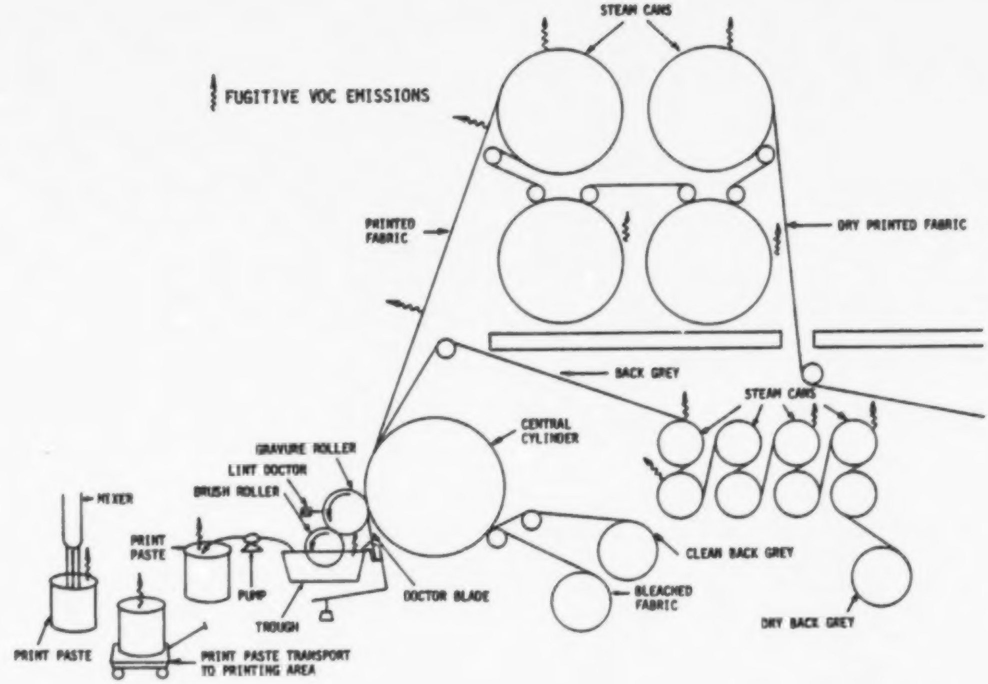

STEAM CANS
FUGITIVE VOC EMISSIONS
PRINTED FABRIC
DRY PRINTED FABRIC
BACK GREY
STEAM CANS
CENTRAL CYLINDER
GRAVURE ROLLER
LINT DOCTOR
MIXER
BRUSH ROLLER
PRINT PASTE
PUMP
TROUGH
DOCTOR BLADE
CLEAN BACK GREY
BLEACHED FABRIC
DRY BACK GREY
PRINT PASTE
PRINT PASTE TRANSPORT TO PRINTING AREA

FIGURE 6-4 - ROTARY SCREEN PRINTING LINE AND ASSOCIATED DRYING AND CURING OVEN

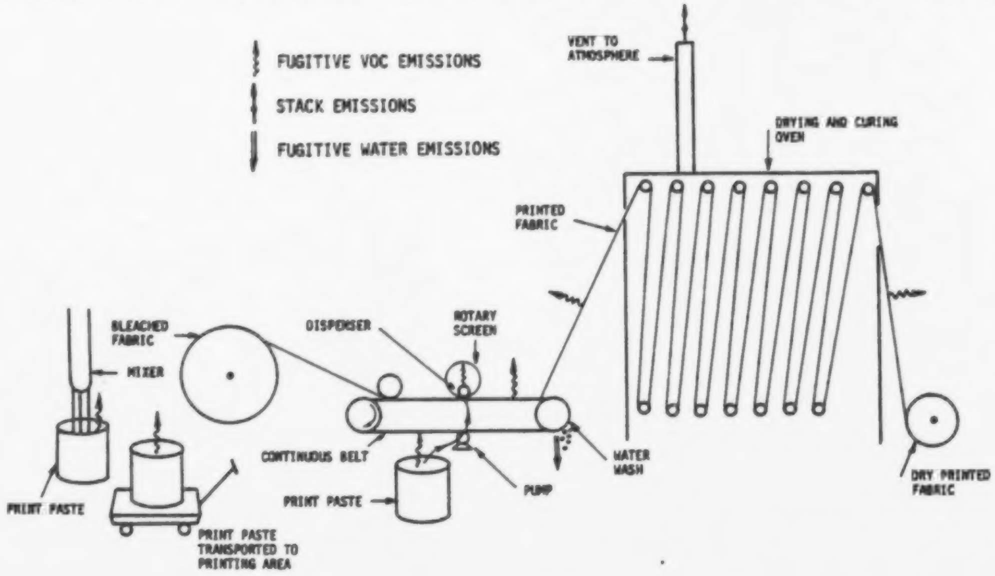

FUGITIVE VOC EMISSIONS
STACK EMISSIONS
FUGITIVE WATER EMISSIONS
VENT TO ATMOSPHERE
DRYING AND CURING OVEN
PRINTED FABRIC
BLEACHED FABRIC
DISPENSER
ROTARY SCREEN
MIXER
CONTINUOUS BELT
WATER WASH
PUMP
PRINT PASTE
DRY PRINTED FABRIC
PRINT PASTE
PRINT PASTE TRANSPORTED TO PRINTING AREA

TABLE 6-1

MODEL PRINTING LINE PARAMETERS

	MPL 1	MPL 2
1. Fabric		
A. Type (% woven/% knit):	70/30	70/30
B. Fiber (% natural/% man-made):	30/70	30/70
C. Average weight, kilograms/meter:	0.13	0.13
(pounds/yard):	(0.25)	(0.25)
D. Average width, centimeters:	137	137
(inches):	(54)	(54)
2. Print Pastes		
A. Annual print paste consumption, megagrams (tons):	379 (417)	379 (417
B. Organic solvent content, megagrams (tons):	114 (125)	19 (21)
C. Organic solvent (%):	30	5
3. Production Data		
A. Capacity utilization (%):	84	84
B. Operating efficiency (%):	37	37
C. Average line speed, meters/minute:	41	41
(yards/minute):	(45)	(45)
D. Annual fabric production, meters (yards) x 10^6:	5.4 (5.0)	5.4 (5.0)
4. Drying Process		
A. Type of drying:	Enclosed steam cans	Drying oven
B. Fuel:	No. 6 fuel oil	Natural gas
C. Temperature:	116°C (240°F)	163°C (325°F)
D. Exhaust flow, m^3/minute:	255	240
(ft^3/minute):	(8,500)	(8,000)
5. Estimated VOC Emissions from Drying		
A. Annual VOC emissions, megagrams:	98	16
(tons):	(108)	(18)
B. VOC emissions per operating hour, kilograms (pounds):	53 (117)	9 (20)
C. VOC exhaust stream concentration, parts per million:	1,240	207

MPL = Model Printing Line.

There are, however, a few fabric printing plants that use print pastes with a weighted average organic solvent content of 30 to 45 percent by weight (which can go up to 60 percent in some cases). In most cases, it appears these plants have established a special market for their products (the printing of very dark colors with a soft feel or "hand") and it does not appear that these plants could switch to a lower organic solvent print paste and still maintain this special market niche.

Add-on VOC Emission Control Systems

The only technically feasible add-on VOC control technique appears to be incineration. The high moisture content of the exhaust stream associated with the drying of printed fabric leads to freezing problems in the liquid nitrogen condenser stage of inert condensation recovery systems.14) The relatively high vapor pressure of the organic solvents used in fabric printing operations and the low VOC concentration in the drying exhaust stream cause combination cooler/condenser and electrostatic precipitator systems to have a low VOC removal efficiency.15,16) Activated carbon adsorption systems may be applicable to fabric printing VOC control but this has not yet been verified experimentally.

Thermal incineration of VOC emissions is a frequently used VOC emission reduction technique that is applicable to many types of VOC emissions and industrial processes. In a thermal incinerator, a burner located at the inlet of a thermal incinerator maintains a temperature of 649 to 871°C (1200 to 1600°F). Contaminated air enters through the burner flame zone and is retained in the combustion zone for about 0.50 to 0.75 second. The VOC emissions in the exhaust stream are oxidized in the combustion chamber and the hot combustion gases are exhausted through a stack. The main disadvantage of incineration is the large amount of auxiliary fuel that is required to maintain the high temperatures necessary for oxidation of VOC emissions.

An effective means of reducing auxiliary fuel costs with incineration is by recovery of useful heat from the incinerator unit. Some applications of this heat include preheating the dryer inlet air, preheating the dryer exhaust before it enters the incinerator, and producing steam for building heat or production processes. In most industries, heat is recovered through recuperative shell and tube, air to air heat exchangers, or by regenerative heat wheels. Recuperative heat recovery up to 70 percent is achievable through the proper design of the thermal incinerator and associated heat recovery system.17)

Control cost estimates have been developed for the installation of a thermal incineration system with 70 percent recuperative heat recovery capability on each of the two model printing lines presented previously. The total installed capital cost and total annualized cost for the thermal incineration systems are presented in Table 6-2. As indicated in Table 6-2, the retrofit penalty and hooding, ducting, and enclosure costs associated with MPL 1 are higher than those associated with MPL 2. This is due to the fact that MPL 1 uses steam can drying which is more difficult to retrofit and enclose compared with the industrial drying oven used for MPL 2. However, the higher VOC concentration of the drying exhaust streams for MPL 1 as compared with MPL 2 results in a lower net fuel requirement for the thermal incineration system, and, therefore, an incinerator for MPL 1 would have a lower operating cost than MPL 2. Incinerator equipment costs are an average based on quotes from three thermal incinerator manufacturers.18,19,20) Hooding, ducting, and enclosure costs are estimates from a sheet metal working contractor.21) The fuel requirements were based on energy use calculations. Operating and maintenance labor, retrofit penalties, installation costs, capital recovery factors, and taxes, insurance, and administration factors are from standard references.22)

REGULATORY STATUS

State regulations pertaining to the reduction of VOC emissions from fabric printing operations are summarized in Table 6-3. State regulatory agencies have expressed uncertainty about the applicability of these VOC emission control regulations to fabric printing operations.23,24)

TABLE 6-2

CONTROL COSTS FOR THERMAL INCINERATION SYSTEMS WITH 70 PERCENT RECUPERATIVE HEAT RECOVERY CAPABILITIES

	MPL 1	MPL 2
Equipment cost	$145,000	$145,000
Installation costs	88,000	88,000
Retrofit penalty	64,000	46,000
Hooding, ducting, enclosures	45,000	20,000
Total installed capital cost	$342,000	$299,000
Direct		
Operating labor	$ 4,000	$ 4,000
Maintenance labor	4,000	4,000
Net fuel	16,000	24,000
Electricity	1,000	2,000
Subtotal	$25,000	$34,000
Indirect		
Capital recovery[a]	$56,000	$49,000
Taxes, insurance & administration[b]	14,000	12,000
Subtotal	$70,000	$61,000
Total annualized cost[c]	$95,000	$95,000

[a] Capital recovery factor of 16.275 percent of total installed capital cost. Based on 10 year life of incinerator and 10 percent interest rate.

[b] Four percent of total installed capital cost.

[c] Direct subtotal + indirect subtotal.

MPL = Model Printing Line.
Note: All costs are rounded to the nearest $1,000.

TABLE 6-3

SUMMARY OF STATE VOC EMISSION REGULATIONS[a]

State	Summary of Regulation
Alabama	No regulation unless the source emits over 100 tons per year of VOC. If greater than 100 tons per year of VOC, then source has to apply BACT.[b]
Delaware	No applicable regulation.
New York	Fabric printing operations may be covered by regulation for fabric coating operations, depending on percent of coverage of material. This only applies to sources that emit greater than 100 tons per year of VOC.
Georgia	No applicable regulation. If the source emits greater than 100 tons per year of VOC, or if it is a new source, then BACT must be met for PSD[c] requirements.
South Carolina	Regulation for roller printing which sets a VOC emission limit of 550 pounds per day or 150 pounds per hour. This may be applicable to fabric roller printing operations.
North Carolina	General hydrocarbon regulation which limits emissions of photochemically reactive materials to 40 pounds per day or an emission reduction of 85 percent.
Florida	No applicable regulation.
Maine	Any existing source that has the potential to emit more than 100 tons per year of VOC must reduce emissions by 90 percent. There are no exemptions, and compliance is on a source by source basis.
New Jersey	No applicable regulation.
Connecticut	No applicable regulation.
Pennsylvania	No applicable regulation.
California	No applicable regulation.
Virginia	No applicable regulation.
Massachusetts	No applicable regulation.
Rhode Island	A general regulation on organic solvents. This regulation would probably apply to the organic solvents used in fabric printing print pastes.

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[a] This table addresses State mass emission rate regulations for the control of VOC emissions. States have "odor" and "nuisance" regulations that may be applicable to the control of VOC emissions from fabric printing operations.

[b] Best Available Control Technology.

[c] Prevention of Significant Deterioration.

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16. Memo from Ryan, Ron, GCA/Technology Division, to Viconovic, George, GCA/Technology Division. December 15, 1980. Vaporization and condensation of fabric printing solvents.

17. Memo from Mascone, David C., EPA:CPB, to Farmer, Jack, EPA:CPB. June 11, 1980. Thermal Incinerator Performance for NSPS.

18. Telecon. Viconovic, George, GCA/Technology Division, with Sales Representative, Combustion Engineering. November 18, 1980. Thermal incinerator costs.

19. Telecon. Viconovic, George, GCA/Technology Division, with Sales Representative, Peabody International Inc. November 18, 1980. Thermal incinerator costs.

20. Telecon. Viconovic, George, GCA/Technology Division, with Sales Representative, John Zink Inc. November 19, 1980. Thermal incinerator costs.

21. Telecon. Viconovic, George, GCA/Technology Division, with Hamlin, Robert, Hamlin Sheet Metal Company. November 19, 1980. Sheet metal cost estimates.

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SECTION 7

FLARES

PROCESSES AND EMISSIONS

Flares are used for the disposal of combustible waste gases. Their use is most commonly associated with petroleum refineries but they are also used in petrochemical plants, oil fields, steel mills, sewage disposal plants, and could be necessary in coal gasification plants. Three broad classifications of operational conditions are associated with the use of flares. These are (1) process start-up and shutdown venting, (2) minor operational upsets not causing unit or plant shutdown, and (3) emergency release of process materials as a result of power failure or major equipment failure. An example of the first use would be controlled venting of a vessel prior to performing maintenance; the second category could include flaring of gases from leaking pressure relief valves tied into a manifold system; and the last category could cover the massive diversion of the full process flow. From an operational point of view, flares can be distinguished from thermal incinerators by the requirement to operate under a wide range of conditions. Flares designed to handle emergency releases could be required to handle gas flows ranging from several hundreds of cubic meters over a relatively short period of time. Obviously they must be designed to handle the maximum flow possible under worst-case conditions. Further, these gases may range from hydrogen-rich reformer gases to liquefied petroleum gases.

True flares are classified as either elevated or ground-level. Simple burning pits have also been utilized but their use is generally reserved for extremely large gas flows under catastrophic conditions when the design capacity of the primary flare is exceeded. The elevated flare is the most commonly used type for emergency purposes. The taller elevated flares require a support structure which increases costs, but can be located relatively close to other units and still meet the distance standards associated with radiant heat transfer from the open flame at the tip of the flare. Further, in the case of a flame-out, the flammable gases are not released, even momentarily, at ground level.

Modern flares must be designed to be safe, minimize noise, and be smokeless. The essential parts of a flare are the burner, the stack, seal, liquid trap, controls, pilot burner, and ignition system. A simplified sketch of a typical elevated flare is given in Figure 7-1. A typical refinery blowdown system used in conjunction with the flare is shown in Figure 7-2.

From an air emissions point of view, the principal design and operational objective associated with waste gas flares has been the achievement of smokeless operation. Little attention has been given to the systematic evaluation or control of VOC emissions. The control problem associated with smokeless operation is the injection and thorough mixing of the proper amount of combustion air in order to eliminate or minimize those flame reactions which lead to the formation and agglomeration of soot nuclei. This is not easily done in a relatively simple flare which must handle a wide range (up to very large volumes) of flare gas flow rates. Several possible aproaches to introducing and mixing sufficient quantities of combustion air are given below:

- Direct Air Injection
    - forced air (mechanical blower)
    - induced air (venturi burners)
- Assisted Air Injection
    - steam jet
    - other inert gas (e.g. N_2)

The most popular smokeless type flare, until recent years, has been the steam assisted type, although some multi-tip induced air flares have also been used. Mechanical (forced air) flares were more costly and difficult to control. As the cost of steam has increased, advanced forced air flares have gained in popularity. The use of compressed nitrogen or other inert gas air injection methods have not been cost competitive.

Steam injection type elevated flares predominate in the emergency disposal of combustible waste gases by thermal oxidation. The main action of steam injection is to aspirate air and improve molecular mixing of fuel and air by mechanical and dynamic means. It has also

DIAGRAM OF STEAM-ASSISTED SMOKELESS ELEVATED-FLARE SYSTEM

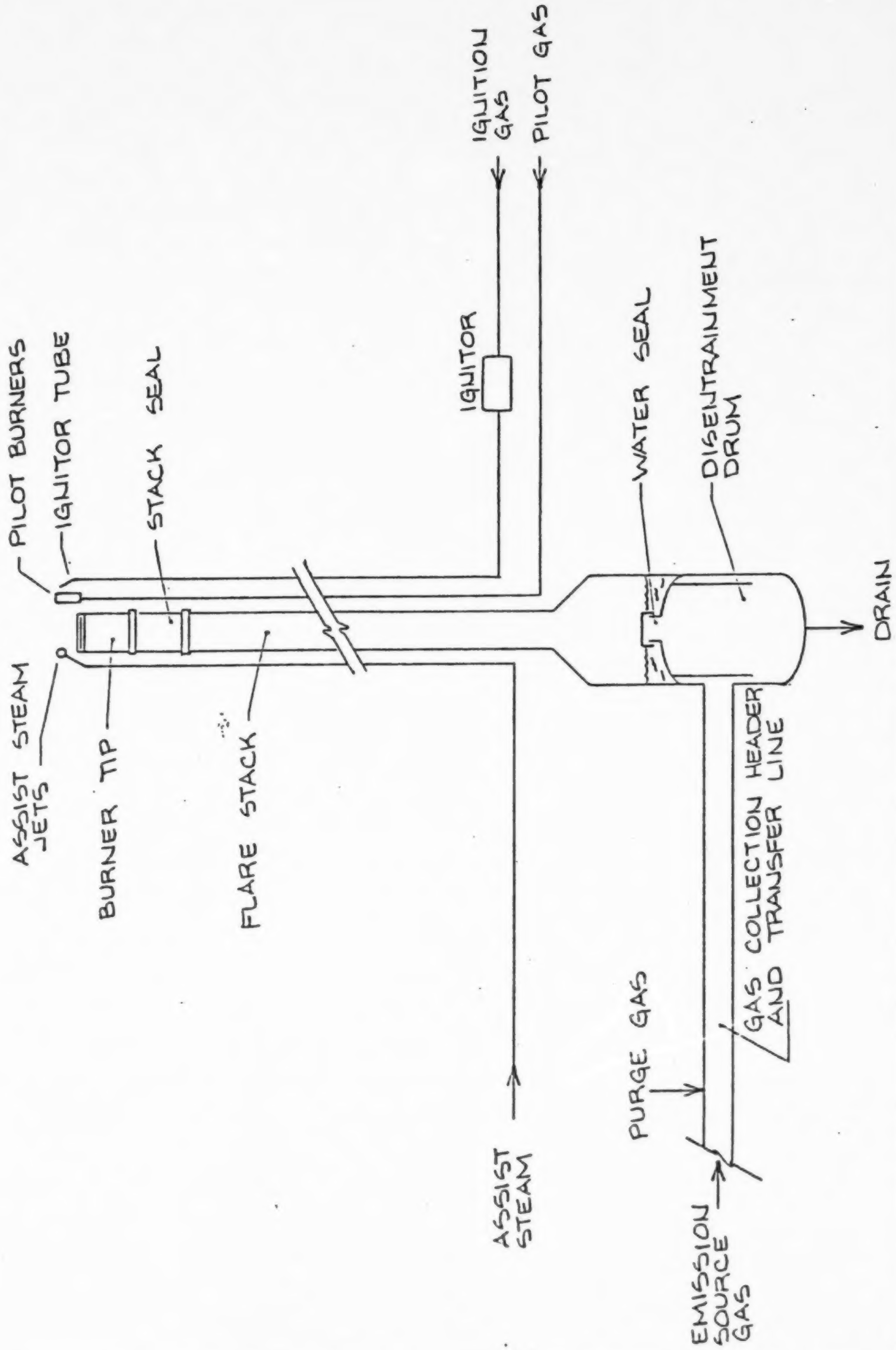
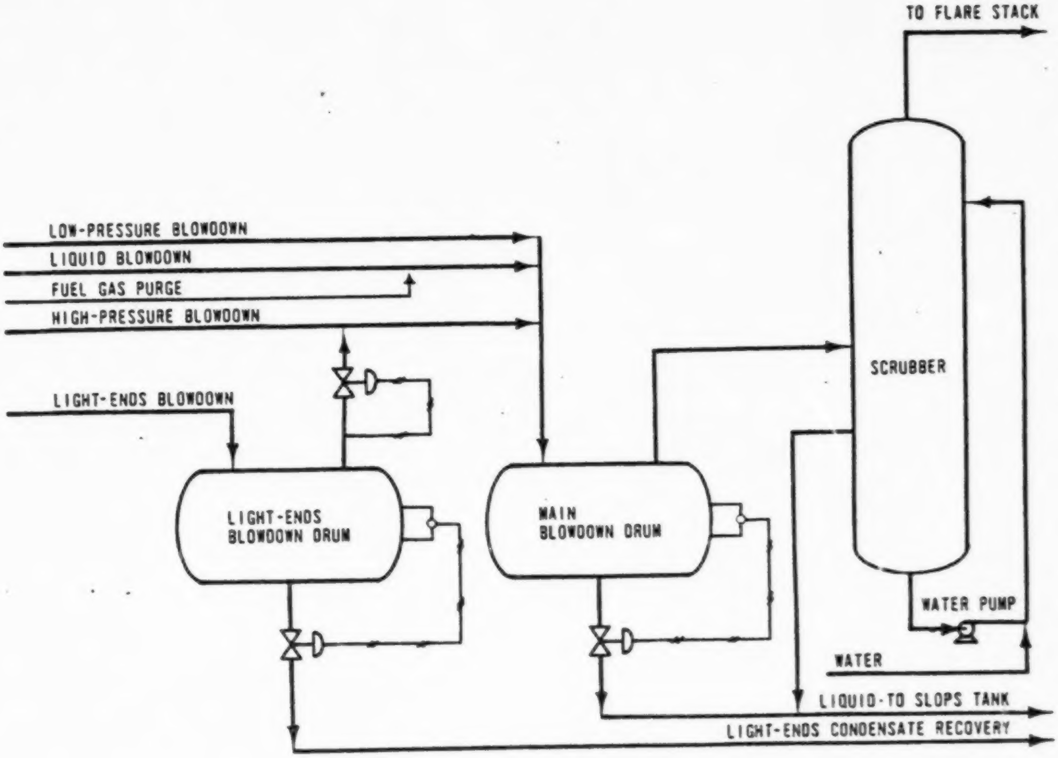

PILOT BURNERS
IGNITOR TUBE
STACK SEAL
IGNITOR
IGNITION GAS
PILOT GAS
WATER SEAL
DISENTRAINMENT DRUM
DRAIN
ASSIST STEAM JETS
BURNER TIP
FLARE STACK
GAS COLLECTION HEADER AND TRANSFER LINE
PURGE GAS
ASSIST STEAM
EMISSION SOURCE GAS

FIGURE 7-2

TYPICAL MODERN REFINERY BLOWDOWN SYSTEM


TO FLARE STACK
LOW-PRESSURE BLOWDOWN
LIQUID BLOWDOWN
FUEL GAS PURGE
HIGH-PRESSURE BLOWDOWN
LIGHT-ENDS BLOWDOWN
SCRUBBER
LIGHT-ENDS
BLOWDOWN DRUM
MAIN
BLOWDOWN DRUM
WATER PUMP
WATER
LIQUID-TO SLOPS TANK
LIGHT-ENDS CONDENSATE RECOVERY

been suggested that the steam reacts with fuel to form oxygenated compounds that burn readily at relatively low temperatures, and that water gas reactions take place with the same general effect1). Tests conducted recently on an experimental flare tend to show that the effect of steam addition on chemical reactions is slight compared to its dynamic contribution towards better combustion2).

There are a variety of combustion tip designs for elevated flares utilizing steam injection. Variations in method and location of steam injection and location of air introduction are the most significant variables. Siegel2) has illustrated a number of flare head designs (Figure 7-3). In flare heads where air is mixed after the gas exits, the flame stabilizes away from the flare mouth. Flare heads using this design operate at lower temperatures in the tip region, and potentially are less subject to corrosion and clogging of steam jet openings with soot. Premixing type flare heads have better flame stability and have less tendency for soot formation.

Important design factors for steam injected elevated flares include gas flow rate and the ratio of steam to flare gas. The stack gas design velocity should be as high as possible to provide increased turbulence and to prevent flashback. The optimum tip velocity range for one design cited by the Air Pollution Engineering Manual1) is 90 to 120 mps. This velocity will vary with design and gas composition. In order to prevent flame blow-out, the maximum velocity is limited to about 150 mps. The mass ratio of steam to flare gas generally should be in the range of 0.2 to 0.51). In the experimental flare tests reported by Siegel2), the following visual results were observed at different steam to air mass ratios:

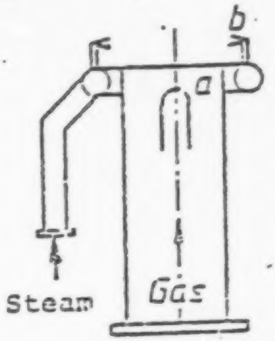
Steam/Gas Ratio (Kg/Kg)	Flame Appearance
0.17	slightly sooty peaks
0.38	soot-free
0.52	almost non-luminous

At ratios over 1.0, carbon monoxide concentrations began to increase, but at ratios as high as about 1.8 there was little increase in unburned hydrocarbon. It should be noted that the tests conducted by Siegel

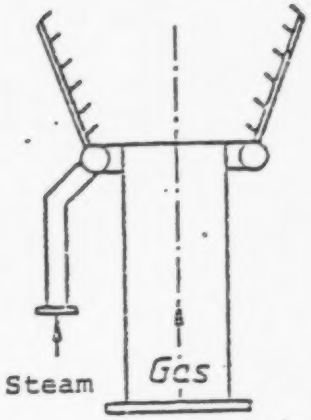
FIGURE 7-3

DIFFERENT DESIGNS OF ELEVATED FLARE HEADS 2)

a. Air-admixing after the exit of the gas

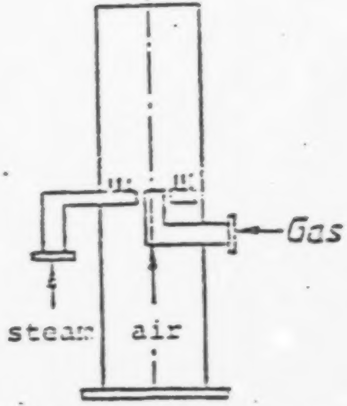

b
a
Steam
Gas

1.a internal steam nozzle
1.b external steam nozzle in one plane

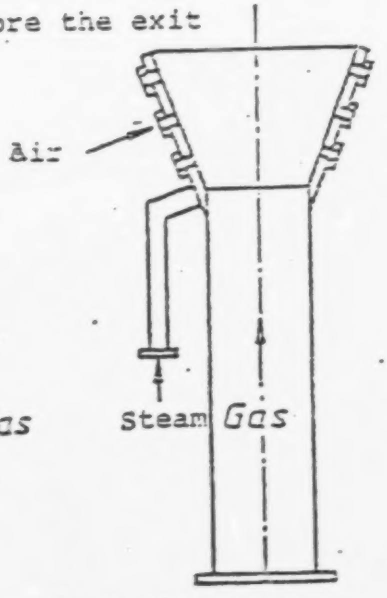


2. external steam nozzles in several planes

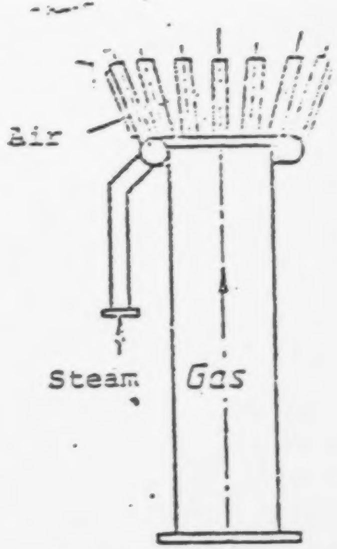
b. Air-admixing before the exit of the gas


Gas
steam
air

3. internal steam- and gas nozzles (Bunsen system)


Air
Steam
Gas

4. annular gap injectors (wall jet)


Air
Steam
Gas

5. injector rods (wall jet)

cannot be considered completely representative of normal flare conditions. The hydrogen concentration of the flare gases was high (mostly between 50 and 64 percent by volume) and the heat content high. Also, the partially premixed flame is not typical of flares in this country. At excessive steam/gas ratios flame cooling could reach the point where combustion no longer takes place. From the above it is apparent that steam flow should be controlled as a function of flare gas flow. This can be done manually or with automatic controls. In the latter case, various means of sensing gas flow and using this parameter to control steam flow have been used. Two variations of flow measurement orifices are shown in Figures 7-4 and 7-5.

Direct air induction using multiple venturi burner sets have been used on some ground flares. These depend on sequentially placing additional burners on-line as flow increases. Both pressure activated valves and water sealed drums set to release at different pressures have been used to add burners to the circuit as flow increases. Figures 7-6 and 7-7 illustrate two different types of multi-jet burners.

One flare construction firm representative3) stated that sales of forced air flares using centrifugal blowers have increased in the past several years due to the rapidly increasing costs of steam. Capacities as high as 100,000 lbs./hr. of flare gas are available. Improved blower controls have aided in making this type of flare more effective in smoke suppression. Figure 7-8 illustrates such a flare.

Data on emissions from flares is very sparse. Tests conducted by Siegel2) showed conversion efficiencies of organic carbon to CO_2 of 98 to 99 percent. Because this was a relatively small test flare and hydrogen content unusually high, the results cannot be considered typical for a full-scale smokeless flare handling relatively high molecular weight hydrocarbons.

FIGURE 7-4

WASTE-GAS FLARE SYSTEM USING ESSO-TYPE BURNER
REGULATED WITH SLOTTED ORIFICE

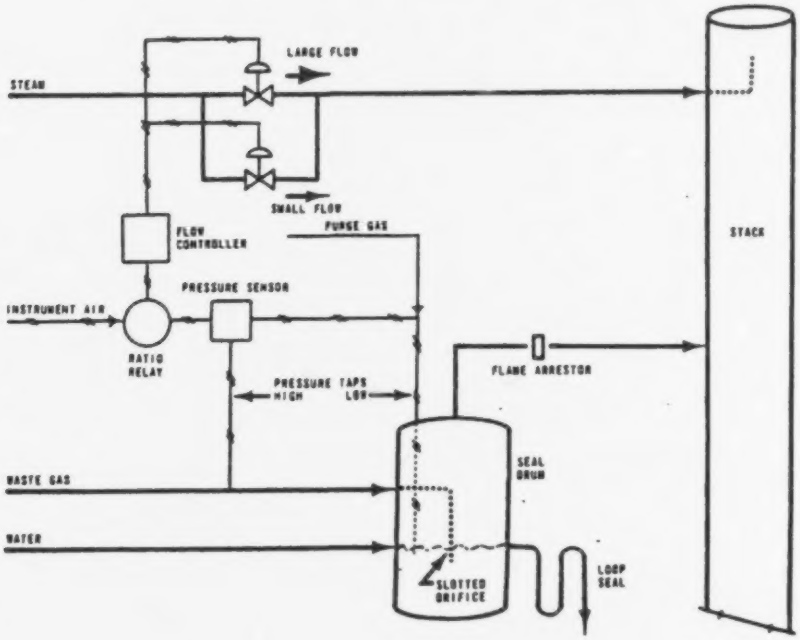
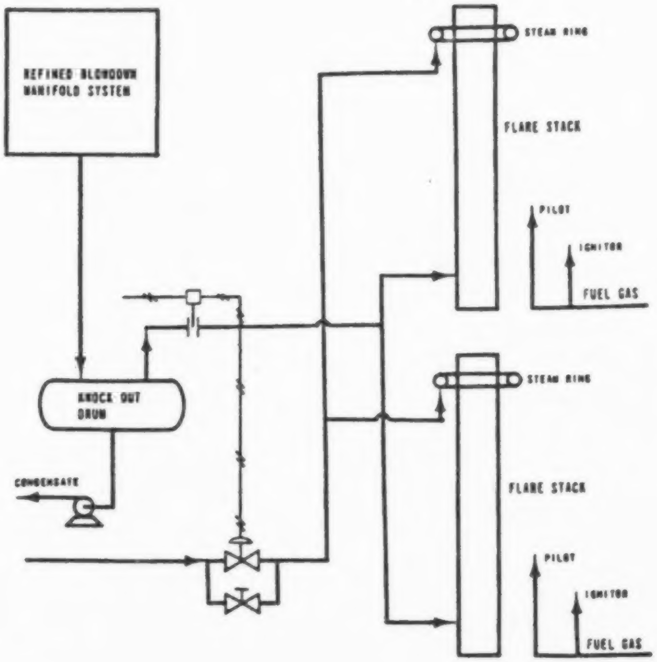

LARGE FLOW
STEAM
SMALL FLOW
FLOW CONTROLLER
PURGE GAS
STACK
PRESSURE SENSOR
INSTRUMENT AIR
RATIO RELAY
FLAME ARRESTOR
PRESSURE TAPS
HIGH
LOW
SEAL DRUM
WASTE GAS
WATER
SLOTTED ORIFICE
LOOP SEAL

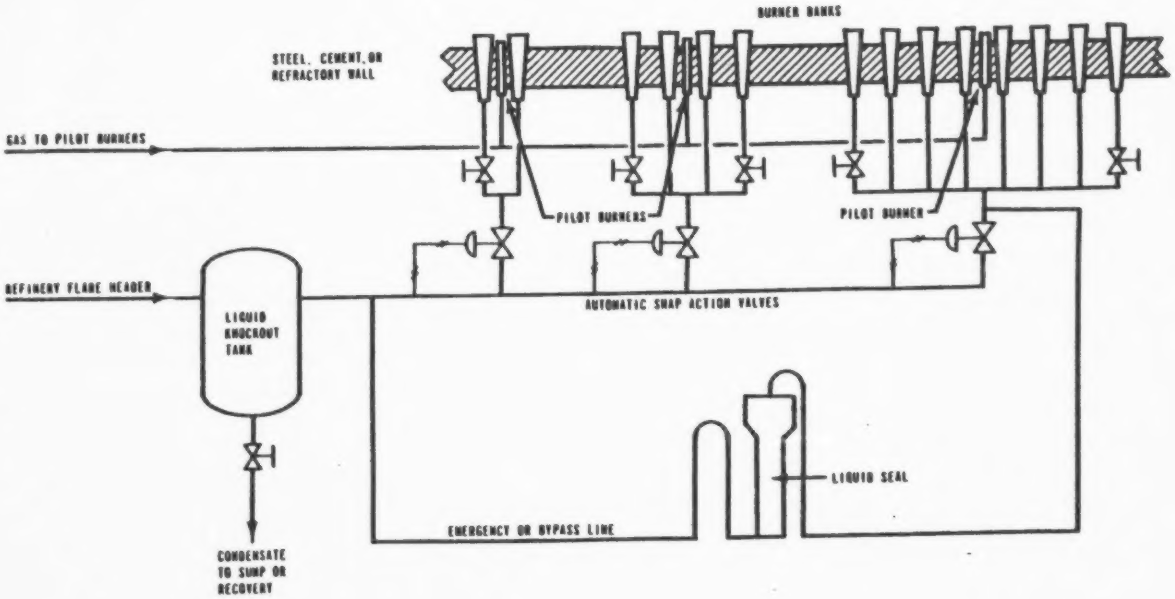
FIGURE 7-5

DIAGRAM OF WASTE-GAS FLARE SYSTEM
USING A SINCLAIR BURNER USING IN-LINE ORIFICE FOR REGULATION


REFINED BLOWDOWN MANIFOLD SYSTEM
STEAM RING
FLARE STACK
PILOT
IGNITOR
FUEL GAS
KNOCK OUT DRUM
CONDENSATE
STEAM RING
FLARE STACK
PILOT
IGNITOR
FUEL GAS

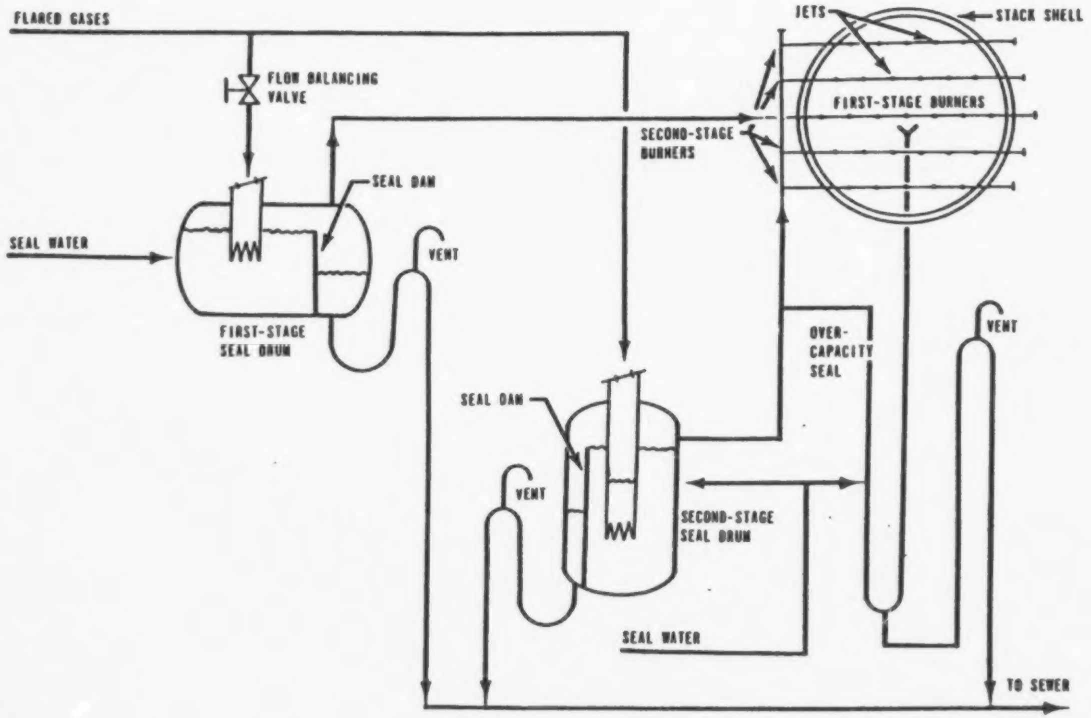
TYPICAL VENTURI GROUND FLARE*

*The ignitors for pilot burners and the warning element for pilot operation are not shown (American Petroleum Institute, 1957).

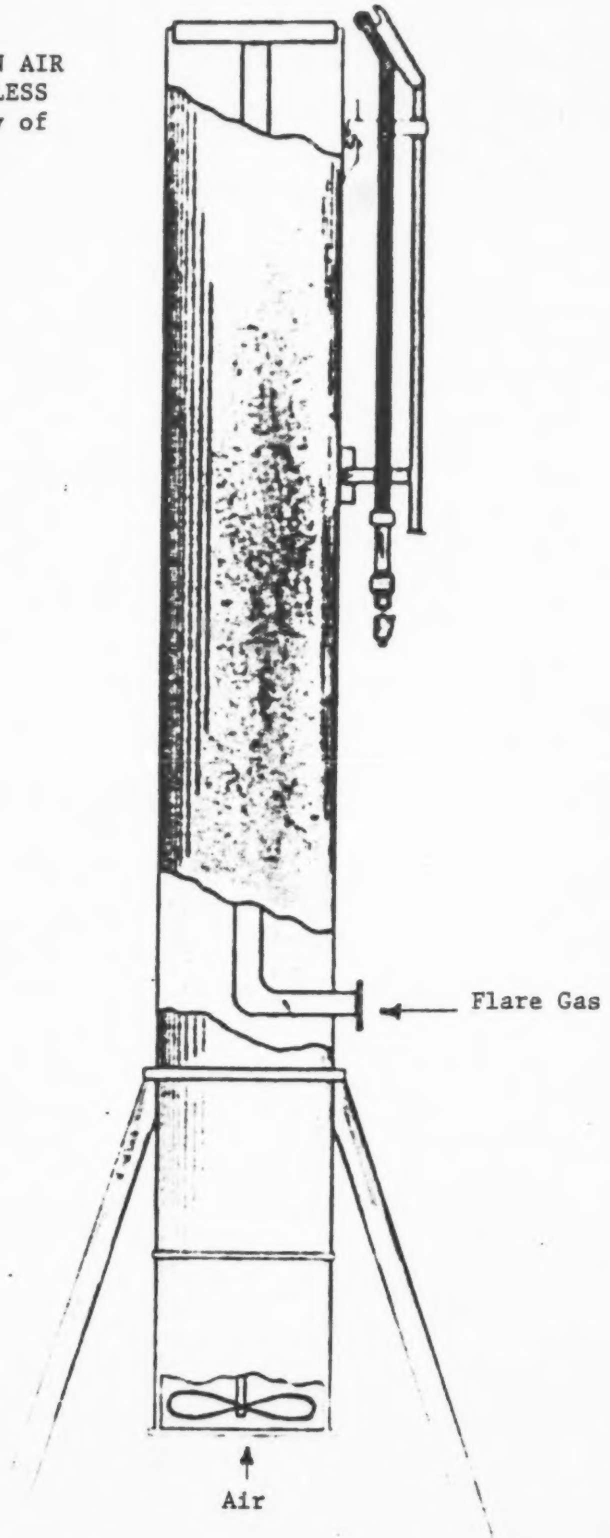

BURNER BANKS
STEEL, CEMENT, OR REFRACTORY WALL
GAS TO PILOT BURNERS
PILOT BURNERS
PILOT BURNER
REFINERY FLARE HEADER
LIQUID KNOCKOUT TANK
AUTOMATIC SNAP ACTION VALVES
LIQUID SEAL
EMERGENCY OR BYPASS LINE
CONDENSATE TO SUMP OR RECOVERY

FLOW DIAGRAM OF MULTI-JET FLARE SYSTEM*

*Miller et al., 1956)


FLARED GASES
FLOW BALANCING VALVE
SEAL WATER
SEAL DAM
FIRST-STAGE SEAL DRUM
VENT
JETS
STACK SHELL
FIRST-STAGE BURNERS
SECOND-STAGE BURNERS
OVER-CAPACITY SEAL
VENT
SEAL DAM
VENT
SECOND-STAGE SEAL DRUM
SEAL WATER
TO SEWER

SCHEMATIC OF AN AIR ASSISTED SMOKELESS FLARE (Courtesy of John Zink Co.)


Flare Gas
Air

CONTROL TECHNOLOGY

Design of flares to meet existing air pollution emission standards has been directed towards achieving reliable smokeless operation and not to reduction of VOC emissions. Information presented in the above section indicates VOC emissions per unit of fuel burned can be higher from a smokeless flare than those from a properly designed boiler. Further, it is possible for VOC emissions to increase without concurrent smoke formation in steam assisted flares if the steam/fuel ratio is too high.

Several alternatives appear to be possible for reducing overall emissions from flare operation. Not all are feasible or even possible at all locations. These alternatives are listed below:

1. Process Changes
   - Reduce potential for flaring by improved process control.
   - Reduce quantities of material routinely flared by substituting vapor recovery systems.
   - Utilize more of the flare gases in fuel gas systems where combustion takes place in well controlled boilers or furnaces.
2. Flare Design Changes
   - Improve combustion by improvement in burner design, including staged use of burners and better combustion air mixing.
   - Provide closer control of steam/flare gas ratio over wide range of flare gas rates.
   - Consider other methods of combustion air introduction such as blowers.

Additional information is necessary to quantify emissions from flares and to determine the most effective control measures. The U.S. EPA has two active contracts to obtain such information4). The first is a short-term contract to develop test methods. The second is a longer-range program to determine flare efficiency under various conditions. No data from these programs are yet available.

In a study for the U.S. EPA conducted by I.T. Enviroscience5) of the synthetic organic chemicals manufacturing industry (SOCMI), alternative means of handling flare gases were examined. This report suggests that energy and cost aspects of flaring make the use of flare gases as fuel an attractive option where technologically feasible. Cost benefit curves for elevated flares, ground flares, and a fuel gas system are reproduced in Figures 7-9, 7-10, and 7-11. Data should be used for comparison as they were developed using a particular design basis.

STATUS OF REGULATORY ACTION

There are no source-specific rules pertaining to VOC emissions from flare gas systems at the federal, state, or local level. Many states and local agencies, however, regulate smoke from flares under general prohibitions on opacity of visible emissions. To some extent these regulations indirectly serve to reduce VOC emissions as compared to uncontrolled smoke-producing flares.

The California Air Resources Board has conducted a survey of flare use in California, but a proposed model rule has not yet been developed.

FIGURE 7-9

COST EFFECTIVENSS OF VOC DESTROYED BY AN ELEVATED-FLARE SYSTEM$^{5)}$

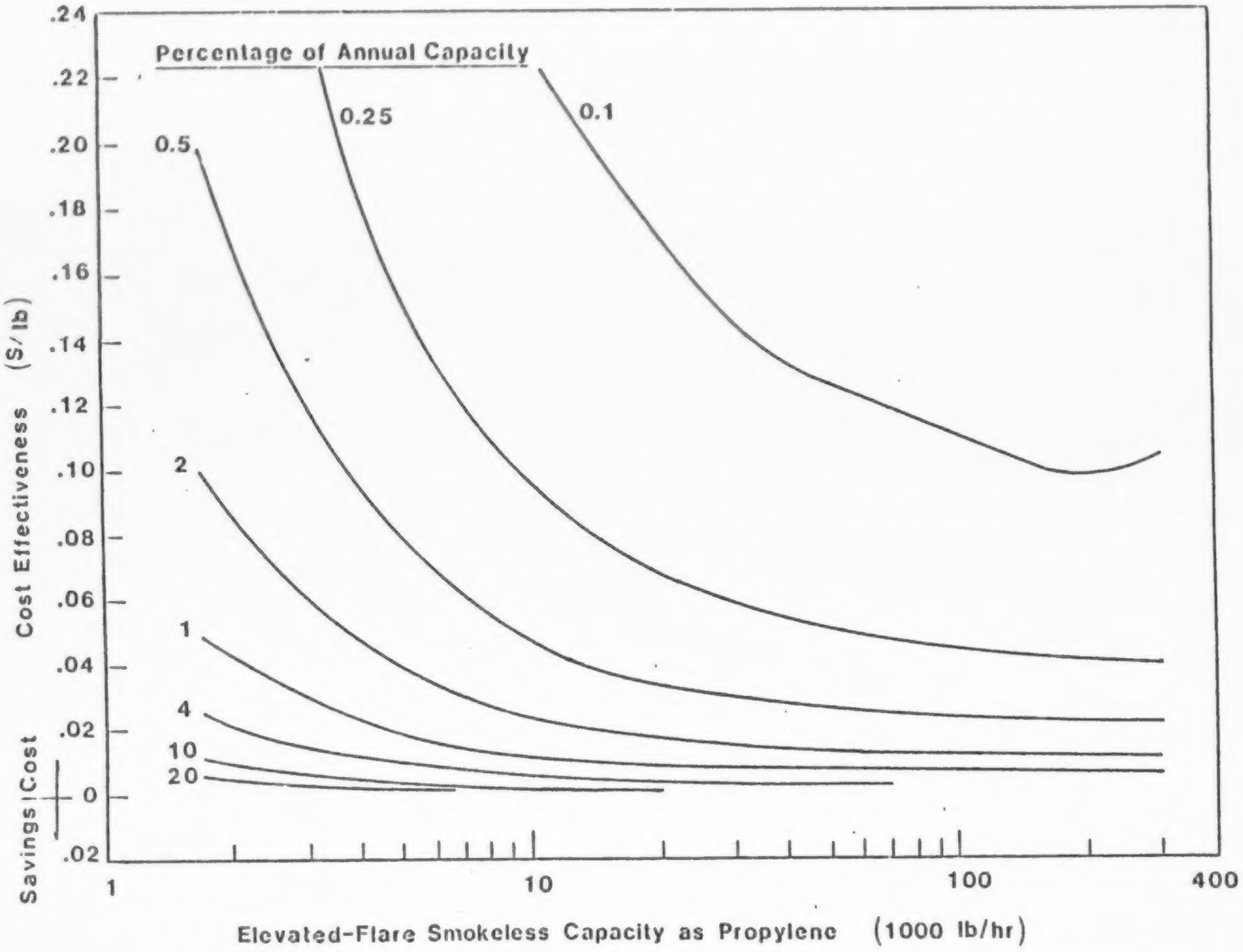


FIGURE 7-10

GROUND-FLARE SYSTEM GROSS ANNUAL OPERATING COST 5)

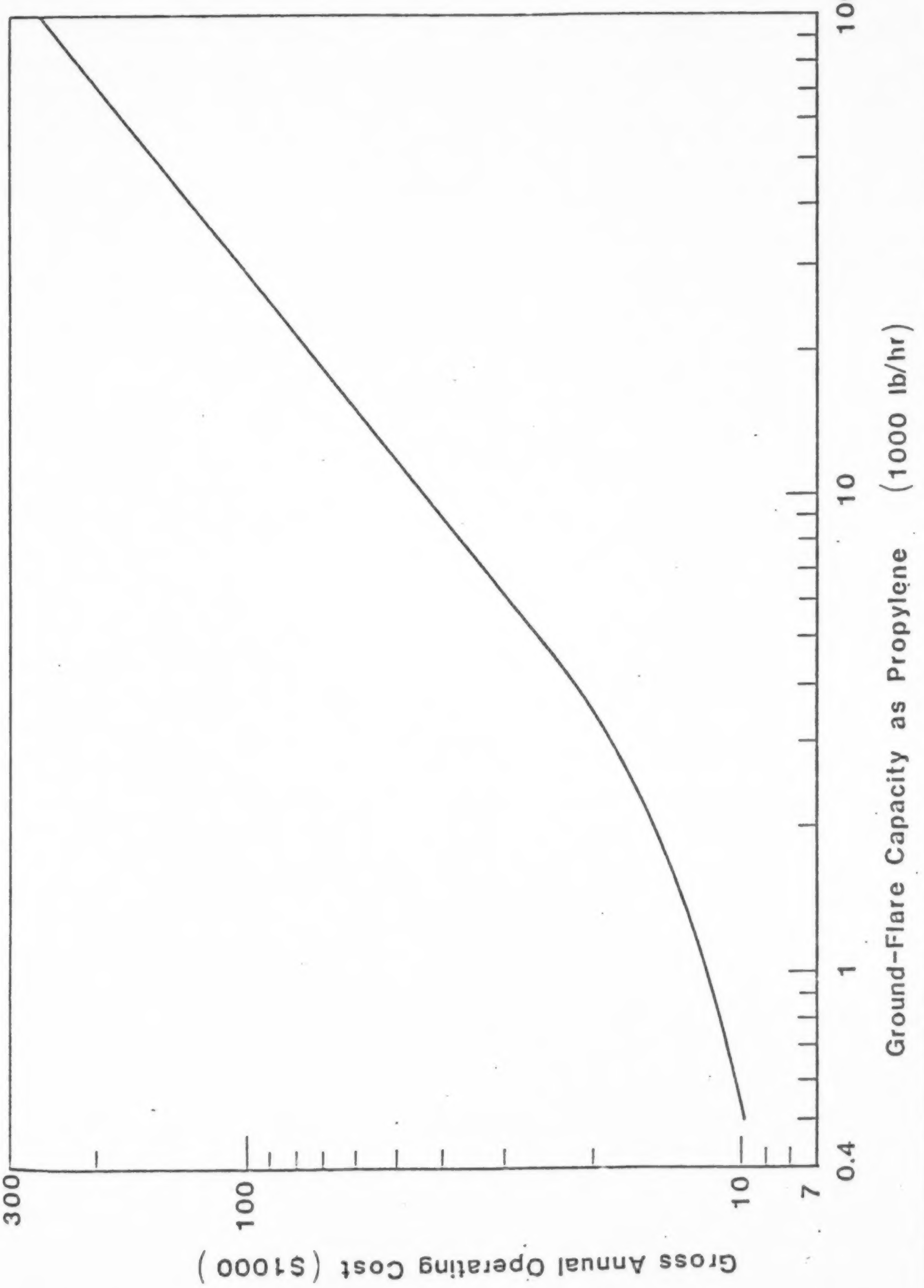
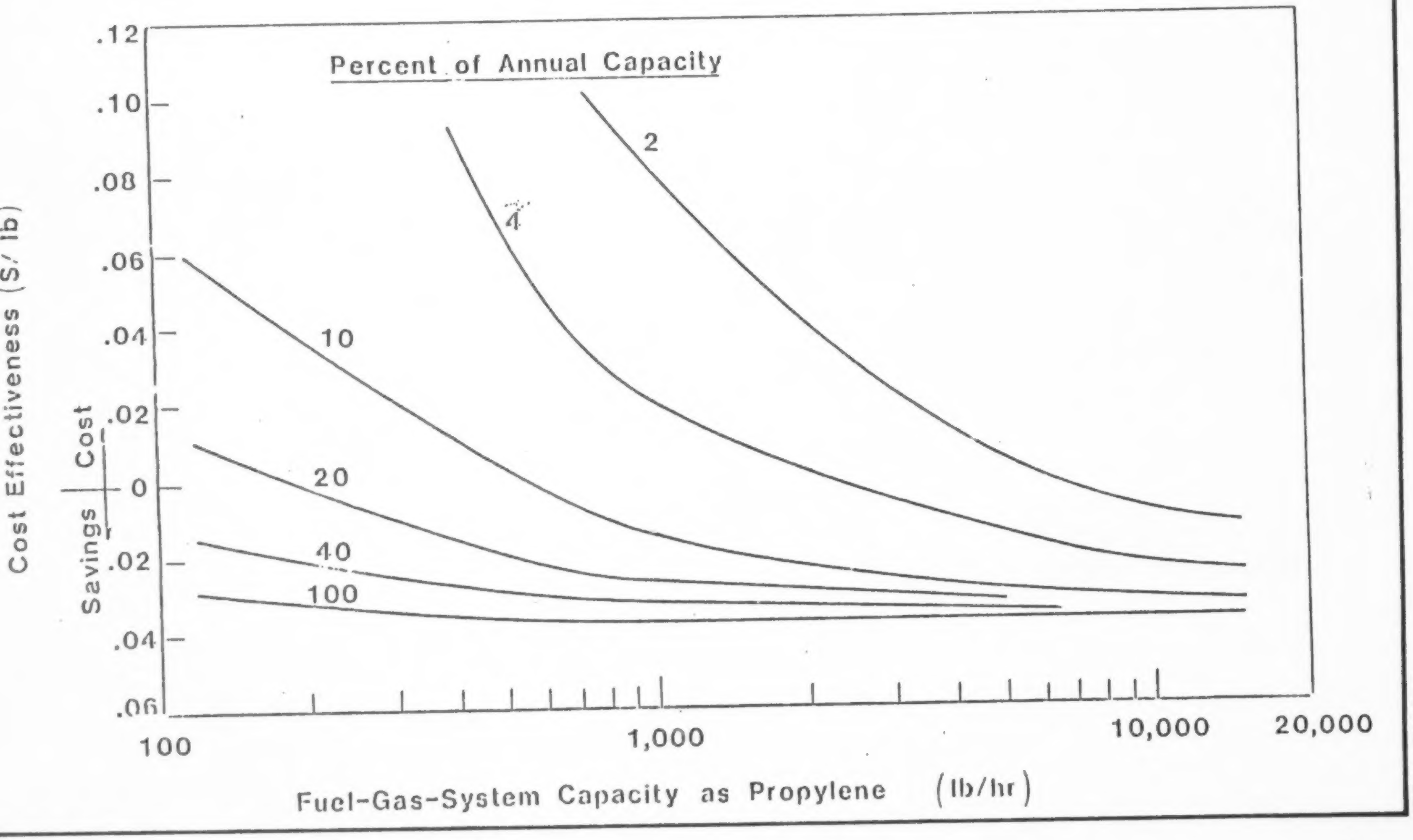


FIGURE 7-11

COST EFFECTIVENESS OF VOC DESTROYED BY A FUEL-GAS SYSTEM5)



REFERENCES

1. "Air Pollution Engineering Manual," AP-40, Second Ed., U.S. EPA, OAQPS, RTP, NC, May 1973.

2. K. D. Siegel, "Degree of Conversion of Flare Gas in Refinery High Flares. Pollutant Emission from Refinery High Flares as a Function of Their Operating Conditions," dissertation for the degree of Ph.D. in Engineering Science at the Chemical Engineering Department of the University in Karlsruhe, West Germany, February 1980.

3. Personal communication from Dick Bell, the John Zink Company, to R. J. Bryan, Engineering-Science, Inc., February 26, 1981.

4. Personal communication between Les Evans, U.S. EPA, and R. J. Bryan, Engineering-Science, Inc., February 3, 1981.

5. "Emission Control Options for the Synthetic Organic Chemicals Manufacturing Industry: Flares and the Use of Emissions as Fuels," prepared by I.T. Enviroscience for the U.S. EPA, OAQPS, ESED, RTP, NC, Contract No. 68-02-2577, August 1980.

SECTION 8

LUBE OIL MANUFACTURING

PROCESSES AND EMISSIONS

The heavy distillates and residues provide heavy oils for various uses such as waxes and lubricating oils. These distillates are also hydrocracked to lighter distillate fuels and gasoline. In 1972, lubricating oils and greases accounted for 67.8 million barrels of the 4,280 million barrels of crude run to stills1). Both solvent extraction and chemical treatment have been standard practices in the upgrading of lubricants. The use of additives (0.001 to 25 percent or more) such as antioxidants, detergents, extreme-pressure agents, antifoam compounds, viscosity index improvers and antiscuff agents are used to improve the performance of most lubricants.

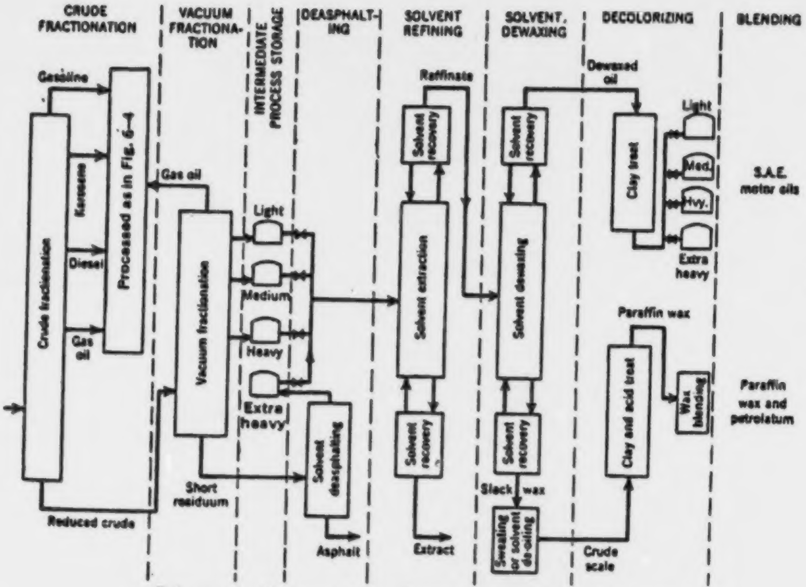
Lubricating oils are manufactured from paraffin-based oils and mixed-base oils. When lubricating oils are produced from the mixed-base oils, they generally require acid or solvent treatment.

Solvent treating or extraction is one of the most widely used processes; however, there are numerous methods and a wide variety of heavy-oil stocks. Figure 8-1 illustrates the general flow of operations presently conducted in lube oil manufacture. The solvent treatment rids the oil of a majority of the dark colored materials. However, the older, more conventional treatments such as clay percolation or contacting usually must also be incorporated.

The Pennsylvanian stocks are finishable by contacting or percolation alone. Both acid and clay treatment are necessary for lube stocks from superior lube crude oil. Catalytic desulfurization and hydrogenation are also suggested as a method of preparing superior raw lubricating oil stocks.

Vacuum distillation in the presence of a small amount of caustic soda, or soda ash, acid treatment and soda ash neutralization of each of the several lube fractions, and percolation clay treatment result in the manufacture of low-cold-test lubricating oils. The lightest lube

SCHEMATIC DIAGRAM OF A REFINERY FOR PRODUCING LUBRICATING OILS


CRUDE FRACTIONATION
VACUUM FRACTIONATION
INTERMEDIATE PROCESS STORAGE
DEASPHALTING
SOLVENT REFINING
SOLVENT, DEWAXING
DECOLORIZING
BLENDING
Gasoline
Kerosene
Diesel
Gas oil
Crude fractionation
Processed as in Fig. 6-4
Reduced crude
Gas oil
Vacuum fractionation
Short residuum
Light
Medium
Heavy
Extra heavy
Solvent deasphalting
Asphalt
Raffinate
Solvent recovery
Solvent extraction
Solvent recovery
Extract
Solvent recovery
Solvent dewaxing
Solvent recovery
Slack wax
Sweating or solvent de-oiling
Crude scale
Dewaxed oil
Clay treat
Light
Med.
Hvy.
Extra heavy
S.A.E. motor oils
Paraffin wax
Clay and acid treat
Wax blending
Paraffin wax and petrolatum

Schematic diagram of a refinery for producing lubricating oils.

Reference 2

fraction, naphtha, is used to dilute the viscous oils before treating. For the lightest oils, the acid ranges from 10 lbs./bbl. to 40 lbs. for the heaviest (150 to 200 viscosity at 210°F), and the range for the soda ash neutralization is from 1 to 3 lbs./bbl.

Batch agitators are usually used for the acid treatment of lube stocks. Table 8-1 presents the various operations of treating oils (the characteristics of which vary greatly). Neutralization with soda ash or caustic is achieved by agitating gently with 3 to 15°Be' caustic until neutral, spraying with hot water or steaming and settling for 4 to 15 hours; several washings and settlings are generally required. The oil can then be brightened by heating to 120 to 200°F by steam coils in an open pan; heating and blowing with air; or by agitating with dry Sil-O-Cel, etc., and filtering. Neutralization by ammonia is becoming increasingly popular since the highly stable emulsions which form during neutralization via caustic or soda do not form with the ammonia method, nor do they form with the clay contact process.

Treatment of lubricating oils by centrifuges or horizontal mixers is frequently done. In this process the oil is heated and mixed with acid for about 10 minutes by a mechanical and/or reaction tank. Water is then added to prepare the sludge, and discharged through the centrifuges. As the sludge accumulates in the hopper, it is continuously pumped to fuel oil mixing tanks or to an acid recovery system.

Lube Oil Hydrotreating Process

Hydrotreating, though not the most conventional method of petroleum product production, yields a full scope of finished single-grade or multigrade lube oils with a wide range yield-viscosity distribution, in addition to valuable byproducts consisting of gasoline, naphtha, kerosine, furnace oil, and waxes (see Figure 8-2).

Makeup and recycle hydrogen along with oil feed are charged to the reactor where viscosity index improvement, desulfurization, denitrogenation, carbon residue reduction, and demetallization are obtained. The bottoms (total lube product) is dewaxed after the hydrogen-rich recycle gas stream is flashed from the reactor effluent and the liquid product

TABLE 8-1

TREATMENT OF OILS

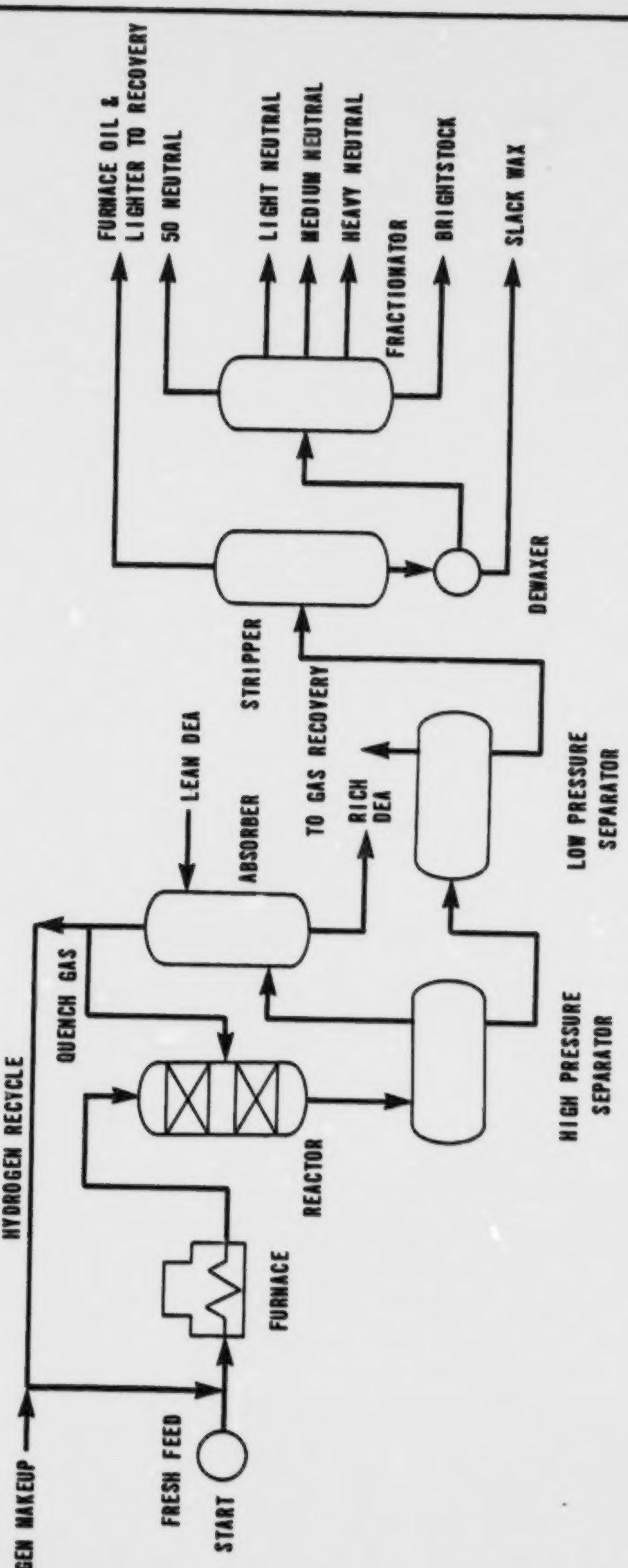
	Distilled Cylinder Stock	Residual Cylinder Stock	225 Neutral	Pale Oils	Average Oils
Refiner	I	I	I	II	III
Pounds water acid, 66°Be', agitate 1/2 hr.	4	32	1	4	2-12
Hours of settle and draw	6	4	2	4	2-31
Pounds acting acid, 66°Be', agitate 1/2-1 hr.	8	---	4	10-18[a]	20-60
Hours of settle and draw	5	---	9	12-20	2-8
Water wash	---	---	(150 gal. per 1,000 bbl.)		Yes
Neutralized by	Clay Contact	Clay Contact	Clay Contact	Caustic	Caustic

a) 98 percent acid.

Reference No. 2

FIGURE 8-2

LUBE OIL HYDROTREATING


HYDROGEN MAKEUP
HYDROGEN RECYCLE
QUENCH GAS
START
FRESH FEED
FURNACE
REACTOR
HIGH PRESSURE SEPARATOR
ABSORBER
LEAN DEA
RICH DEA
TO GAS RECOVERY
LOW PRESSURE SEPARATOR
STRIPPER
DEWAXER
FRACTIONATOR
FURNACE OIL & LIGHTER TO RECOVERY
50 NEUTRAL
LIGHT NEUTRAL
MEDIUM NEUTRAL
HEAVY NEUTRAL
BRIGHTSTOCK
SLACK WAX

Reference 3

is charged to a stripper to remove oil and the lighter products. The various viscosity lube oils are produced by vacuum distillation of the dewaxed oil. The distillation can also be done prior to the dewaxing for other desired fractions.

Process Emissions and Emission Points from Solvent Treating and Hydrotreating

Extraction involves the removal of a component from a liquid by means of the selective solvent action of another liquid. This procedure facilitates the removing of low-viscosity index hydrocarbons, unusable sludges and colored materials from lubricating oil. Generally, the extraction is countercurrent. This presents two difficulties: obtaining solution equilibrium and separating the two immiscible phases. As an example, the extractive refining of lubricating oils with furfural ($C_5H_4O_2$) is illustrated in Figure 8-3. Color bodies, sulfur compounds, and oxygen-containing molecules are effectively removed from lube-oil stock by furfural. As shown in Figure 8-4, of a typical solvent-refining process of lubricating oil, the oil is mixed with the solvent or solvents in an extractor column. Use of the proper solvent, facilitates the separation of the mixture into two layers, one of which is rich in solvent and containing the dissolved impurities (extract), and the other containing little solvent and most of the desirable oil (raffinate). The procedure as presented in Figures 8-3 and 8-4 incorporates the following unit operations when furfural solvent is used:

- Continuous countercurrent extraction of the lubricating stock with furfural at temperatures between 130 and 280°F, depending on the oil used; suitable heat exchangers are provided.
- Continuous separation of the raffinate fraction from the extract fraction.
- Recovery of solvent (furfural) by vacuum evaporation from raffinate or refined oil.
- Stripping by steam distillation of small amounts of remaining solvent from refined oil, giving wet furfural or water solution of furfural.

FIGURE 8-3

FLOWCHART FOR LUBE-OIL REFINING BY FURFURAL EXTRACTION

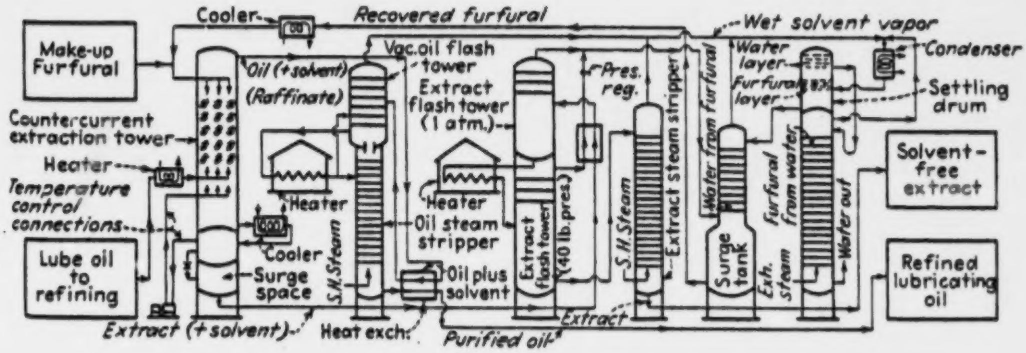
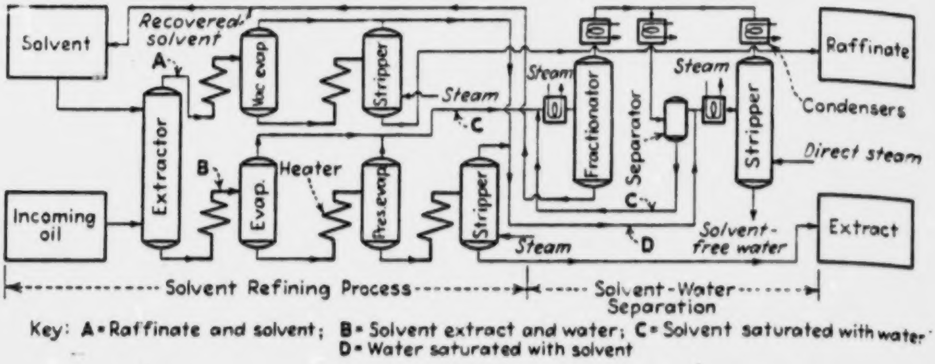

Cooler
Recovered furfural
Wet solvent vapor
Make-up Furfural
Oil (+solvent) (Raffinate)
Vac. oil flash tower
Extract flash tower (1 atm.)
Pres. reg.
Water layer
Furfural layer
Condenser
Settling drum
Countercurrent extraction tower
Heater
Temperature control connections
Heater
Cooler
Oil steam stripper
Surge space
S.H. Steam
Oil plus solvent
Extract flash tower (40 lb. pres.)
S.H. Steam
Extract steam stripper
Water from furfural
Surge tank
Furfural from water
Exh. steam
Water out
Solvent-free extract
Refined lubricating oil
Lube oil to refining
Extract (+solvent)
Heat exch.
Purified oil
Extract

FIGURE 8-4

TYPICAL SOLVENT-REFINING PROCESS EMPLOYING FURFURAL AND PROVIDED WITH SOLVENT-WATER SEPARATION AND RECOVERY


Solvent
Recovered solvent
A
Vac evap
Stripper
Steam
C
Steam
Fractionator
Separator
Steam
Stripper
Condensers
Raffinate
Direct steam
Extractor
B
Evap.
Heater
Pres. evap
Stripper
C
Incoming oil
Steam
D
Solvent-free water
Extract
Solvent Refining Process
Solvent-Water Separation
Key: A = Raffinate and solvent; B = Solvent extract and water; C = Solvent saturated with water
D = Water saturated with solvent

Reference 1

- Recovery of solvent (furfural) from extract by atmospheric and by pressure distillation, this wet solvent (furfural) being the main recovery; fractionation leaves dry solvent behind and ready for re-use.
- Stripping with steam of small amounts of solvent left in the extract, furnishing wet solvent or water solution of solvent.
- Final stripping of solvent from combined aqueous solutions; overhead is chilled, and solvent is conducted to fractionator.
- When furfural is used, solvent is recirculated through the system as many as 15 times each day and with a very small loss, less than 0.03 percent of solvent recirculated.

The calculated solvent losses of less than 0.03 percent of recirculated solvent appear low from an industrial standpoint; however, as is often the case, the larger the operation the greater the solvent emissions to the atmosphere, which if left unchecked, could become sizable. The possible loss locations are the following[4]:

Storage Tanks
Wastewater Treatment
Cooling Towers
Compressor Engines
Stationary Fuel Combustion
Valves
Flanges and Other Connecting Devices
Pump and Compressor Seals
Pressure Relief Devices
Drains, Sumps, Hot Wells
Blind Changing
Sampling
Uncontrolled Blowdown

Closely related to this area of the petroleum industry is the re-refining of various oils used in a number of applications. This process is reputed to be a potential source of considerable volatile organic emissions, however, a contact at Golden Eagle Oil (Los Angeles, California) stated that out of the 50 oil refineries in California, only 3 of them produce lube oil. As for the re-refining of it, it is very nonvolatile by nature, thus not a likely source of VOCs. The re-refining process would involve redistilling and filtering used lube oil, in which case the emission sources would be much the same as those listed previously for the production of lube oil.

Both Standard Oil and Amerada Hess Oil companies confirmed that with hydrotreating to produce lube oil (the newer process), the same typical VOC emission sources exist as with any other method.

CONTROL TECHNOLOGY

In the event that volatile organic emissions are significant enough to warrant specific controls on the lube oil production process, condensers would be a possibility.

According to the EPA report titled "Control Techniques for Volatile Organic Emissions from Stationary Sources"4), condensers have long been used as a successful control method (often with additional control equipment) in abating organic emissions from petroleum refining and petrochemical manufacturing. Even when used as the primary control equipment, condensers are usually followed by a secondary air pollution control system (such as an afterburner) which treats the non-condensible gases and achieves a high degree of overall efficiency4).

STATUS OF REGULATORY ACTIVITIES

Presently there are no rules or regulations on the state or local level regarding emissions from the lube oil production process specifically. The existing regulatory work has centered around volatile organic emissions from the general petroleum industry and is mostly concerned with storage, loading and unloading and disposal of volatile organic compounds.

REFERENCES

1. Shreve, R. Norris, and Brink, Joseph A., Chemical Process Industries. McGraw-Hill, 1977.

2. Nelson, W. L., Chemical Engineering Series, Petroleum Refinery Engineering. McGraw-Hill, 1969.

3. Hydrocarbon Processing, Page 128, September 1980.

4. EPA-450/2-78-022, May 1978, Control Techniques for Volatile Organic Emissions from Stationary Sources.

5. Phone Conversation with Harry Chatfield of the South Coast Air Quality Management District, Dec. 1980.

6. Phone Conversation with Chemical Engineer at Amerada Hess Oil Company, Purvis, Mississippi, Jan. 1981.

7. Phone Conversation with Engineer at Standard Oil, San Francisco, California, Jan. 1981.

8. Phone Conversation with Engineer at Golden Eagle Oil, Los Angeles, California, Jan. 1981.

SECTION 9

OIL AND GAS PRODUCTION STORAGE TANKS

PROCESSES AND EMISSIONS

This source category covers tanks used in oil and gas production fields which produce at least some liquid petroleum. These tanks are utilized in production operations prior to transfer of the field output from the producer to a transporter or refiner. Further, for purposes of this section, we are considering onshore production only.

Onshore petroleum production covers the drilling of wells, the recovery from wells, and the field operations conducted prior to transport of oil and/or gas from the field to refineries or other customers. Wells predominantly producing crude oil are called oil wells, and those primarily producing gas are termed gas wells. However, most oil wells produce some gas, and almost all gas wells produce some liquid hydrocarbons through temperature and pressure changes. This liquid is a condensate and is distinct from crude oil.

Installations in petroleum production fields are conveniently classified as (1) tank batteries, (2) gas sweetening, and (3) natural gas liquids plants (Figure 9-1). We will be concerned principally with the tank batteries. The tank battery receives the gas/water, gas/oil, and oil/water mixtures and separates them into fractions. The gas sweetening unit removes hydrogen sulfide (if any) from the natural gas mixture and further processes it, usually involving a sulfur recovery plant. The natural gas liquids plant is designed to remove hydrocarbons heavier than ethane. The condensate so removed is held in pressurized storage tanks.

In a study for the U.S. Environmental Protection Agency, TRW1) estimated the total number of tank batteries in the United States to be 84,541. The greatest number is in Texas (30,828), followed by California (18,114). Again, for purposes of the TRW study, each battery was assumed to include two tanks. The tanks in a model battery (specified for cost analysis purposes) were assigned a capacity of 75,000 liters

FIGURE 9-1

PRODUCTION OPERATIONS AND ASSOCIATED EMISSIONS*

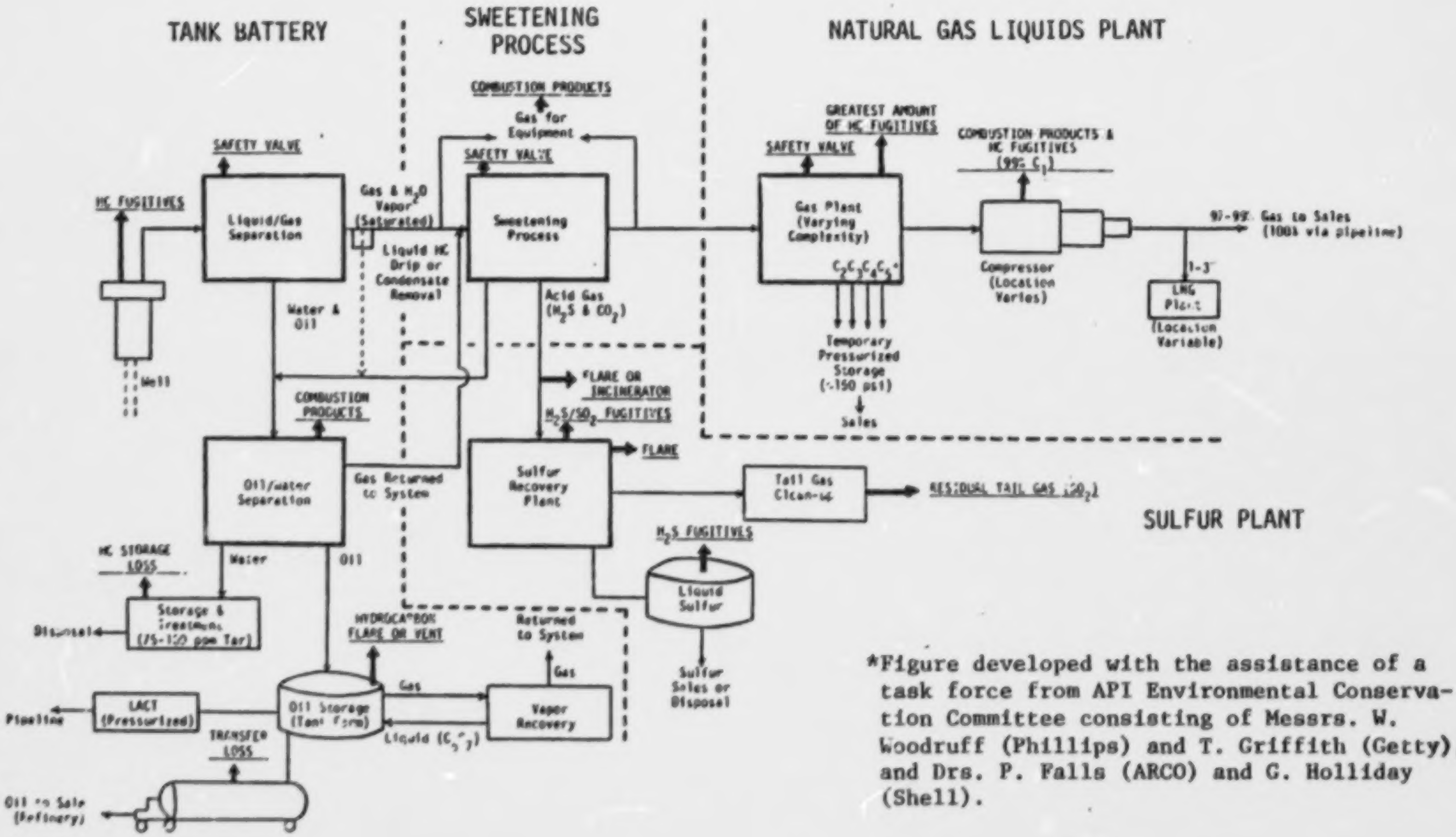

TANK BATTERY
SWEETENING PROCESS
NATURAL GAS LIQUIDS PLANT
SULFUR PLANT
HC FUGITIVES
Well
SAFETY VALVE
Liquid/Gas Separation
Gas & H_2O Vapor (Saturated)
Liquid HC Drip or Condensate Removal
Water & Oil
COMBUSTION PRODUCTS
Oil/water Separation
Gas Returned to System
Water
Oil
HC STORAGE LOSS
Storage & Treatment (75-150 ppm Tar)
Disposal
HYDROCARBON FLARE OR VENT
Gas
Oil Storage (Tank Farm)
Liquid (C_5^+)
Vapor Recovery
Returned to System
LACT (Pressurized)
Pipeline
TRANSFER LOSS
Oil to Sale (Refinery)
COMBUSTION PRODUCTS
Gas for Equipment
SAFETY VALVE
Sweetening Process
Acid Gas (H_2S & CO_2)
FLARE OR INCINERATOR
H_2S/SO_2 FUGITIVES
FLARE
Sulfur Recovery Plant
H_2S FUGITIVES
Liquid Sulfur
Sulfur Sales or Disposal
Tail Gas Clean-up
RESIDUAL TAIL GAS (SO_2)
SAFETY VALVE
GREATEST AMOUNT OF HC FUGITIVES
Gas Plant (Varying Complexity)
$C_2C_3C_4C_5^+$
Temporary Pressurized Storage (~150 psi)
Sales
COMBUSTION PRODUCTS & HC FUGITIVES (99% C_1)
Compressor (Location Varies)
97-99% Gas to Sales (100% via pipeline)
1-3%
LNG Plant (Location Variable)

*Figure developed with the assistance of a task force from API Environmental Conservation Committee consisting of Messrs. W. Woodruff (Phillips) and T. Griffith (Getty), and Drs. P. Falls (ARCO) and G. Holliday (Shell).

Reproduced from best available copy.

(about 470 bbls.). Engineering-Science, in a study of fixed-roof tanks, made tests on oil field tanks ranging from 27,000 liters (170 bbls.) to 16,000,000 liters (100,000 bbls.)2). Many tanks were in the 1,000 bbls. to 2,000 bbls. range, however. Tanks of bolted, riveted, and welded construction are used. Most are fixed cone-roof in design. Very few floating-roof tanks are used in oil fields.

A variety of processing techniques are used to carry out the phase separations conducted in tank batteries. Major items of equipment and their function are listed in Table 9-1. A typical sequence of tank battery units is shown in Figure 9-2. Operations and flow patterns in tanks located in production fields cover a broad range of conditions. Further, crude oil fed to tanks in tank batteries may at times be unstabilized (still contains gas) or near flashing temperatures. In such cases crude oil under slight pressure flashes when introduced into the tanks. In addition to the functional classification of tanks such as wash, knock-out, and storage, they can be classified as to mode of operation. Using this scheme tanks can be classified as batch, continuous or special service. Batch tanks can be filled or emptied but not at the same time. Continuous tanks can be filled and emptied simultaneously. Special service tanks include those where flashing might occur. Figure 9-3 illustrates various tank operations.

Tanks in continuous service are deserving of additional attention because the mode of operation complicates the use of equations used to estimate working loss emissions. This is because the level of the liquid in the tank does not vary as much as a batch tank having the same throughput. Two classes are briefly described. They are Lease Automatic Custody Transfer (LACT) tanks and wash tanks.

The LACT tanks serve a specific function in the oil field. Control of the crude is automatically transferred from the producer to the transporter (or pipeline) as it leaves this tank. The liquid level in these tanks varies between two set points. As liquid enters, the liquid level slowly rises to the upper set point. The high-volume LACT withdrawal pump is actuated and the liquid level falls to the lower set point. The withdrawal pump is turned off, and the procedure starts again.

TABLE 9-1

MAJOR TANK BATTERY PROCESSING EQUIPMENT

Equipment	Primary Function
Two-phase separators	Oil/water and gas separation.
Three-phase separators	Oil and water and gas separation.
Gun barrels	Oil and water separation.
Heater treaters	Oil and water emulsion separation.
Scrubbers or drips	Remove liquids formed in gas lines.
Free water knockouts	Water removal.
Test separators	Isolates wells to determine gas, oil, and water production rates for individual wells.
Oil, water and condensate storage tanks	Self explanatory. Condensate is heavier fractions (C_5+) removed from gas phase following liquid/gas separation.
ACT or LACT units	Automatic or lease automatic custody transfer units used to test and quantify crude oil and/or condensate for sales and lease requirement purposes.

FIGURE 9-2

TYPICAL TANK SEQUENCE IN TANK BATTERY

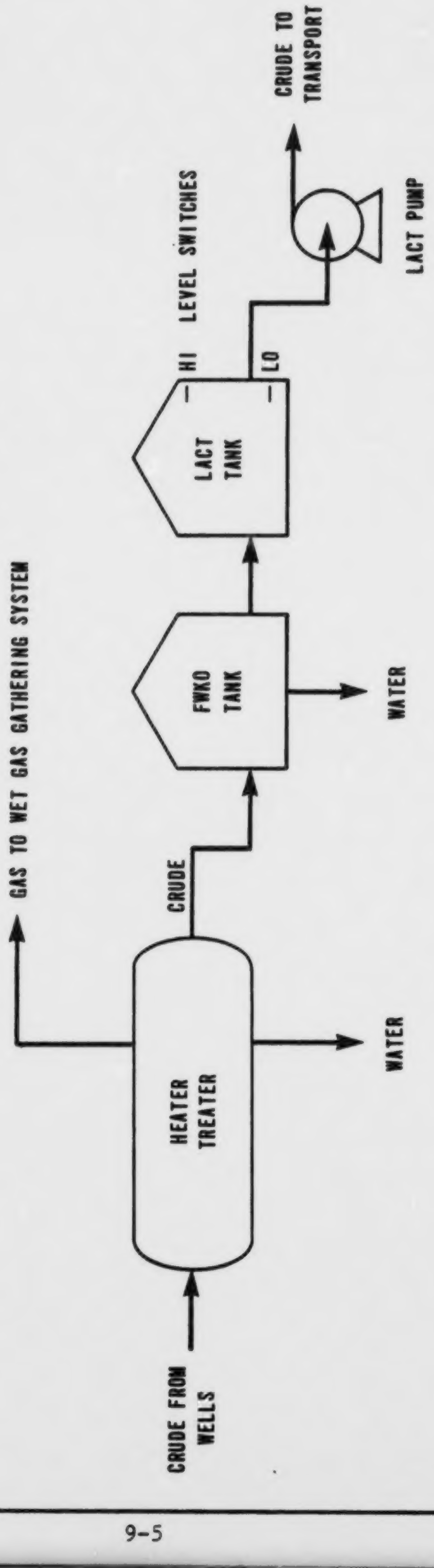
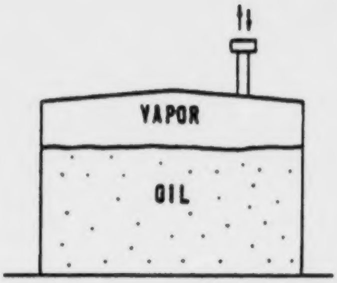

CRUDE FROM WELLS
HEATER TREATER
WATER
GAS TO WET GAS GATHERING SYSTEM
CRUDE
FWKO TANK
WATER
LACT TANK
HI
LO
LEVEL SWITCHES
LACT PUMP
CRUDE TO TRANSPORT

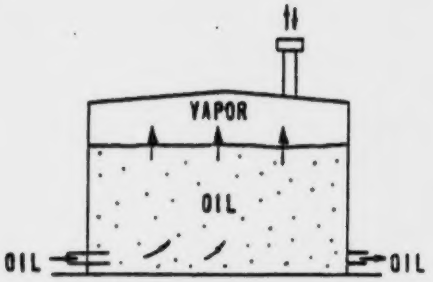
FIGURE 9-3

EXAMPLE OPERATIONS OF FIXED-ROOF TANKS



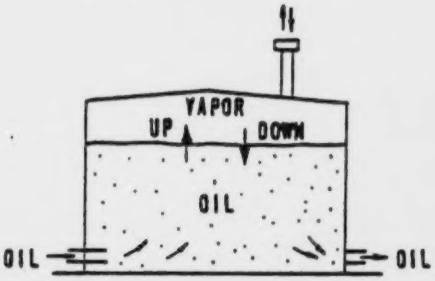
STANDING STORAGE

SUBJECT TO BREATHING LOSS.


VAPOR
OIL
OIL
OIL

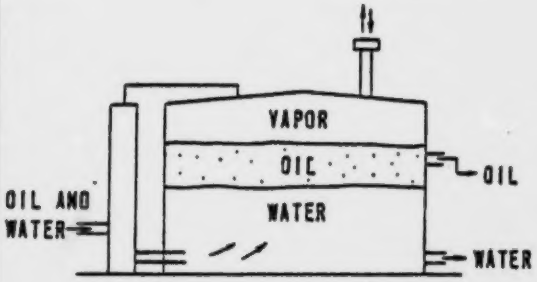
BATCH OPERATIONS

SUBJECT TO CYCLIC FILLING, EMPTYING, AND BREATHING LOSSES.


VAPOR
UP
DOWN
OIL
OIL
OIL

CONTINUOUS OPERATIONS

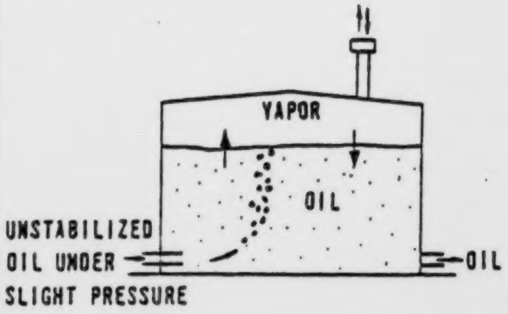
SUBJECT TO FILLING, EMPTYING AND BREATHING LOSSES.


VAPOR
OIL
OIL
OIL AND WATER
WATER
WATER

CONTINUOUS OPERATIONS (WASH TANKS)

SUBJECT TO BREATHING LOSS.

NOTE: IF TANK FEED CONTAINS UNSTABILIZED CRUDE UNDER SLIGHT PRESSURE, THE TANK WILL BE SUBJECT TO FLASHING LOSSES ALSO.


VAPOR
OIL
UNSTABILIZED
OIL UNDER
SLIGHT PRESSURE
OIL

SPECIAL OPERATIONS

SUBJECT TO FLASHING, FILLING, EMPTYING AND BREATHING LOSSES.

Wash tanks are a second particular type of continuous service tank. They separate oil and water in the incoming crude. Oil normally exits the tank in an overflow pipe; therefore, the tanks have a constant liquid level. Frequently, crude comes directly from the various wellheads to the wash tank. The crude mixture contains oil, water, sand, and gases such as nitrogen, and carbon dioxide. The mixture arrives at the wash tank sometimes under pressure (i.e., 30 to 50 psi) and often at elevated temperatures (i.e., 150 to 200°F). A vertical cylinder called a "boot" is sometimes attached to the side of wash tanks. The "boot" relieves any pressure from the crude oil so that flashing of the trapped gases can occur upstream of the wash tank. These gases are piped to the vapor space of the wash tank. From the boot, the oil/water mixture flows into the bottom of the wash tank. The oil floats to the top and overflows into other wash or LACT tanks and the water is drained from the bottom of the tank and discarded into a sump.

EMISSIONS

Emissions from fixed-roof tanks used for crude oil have traditionally been estimated using equations found in API Bulletin 2518[3)] or modification of these equations in AP-42[4)]. These calculations cover breathing losses and working losses. Breathing losses are those due to vapor expelled during the diurnal expansion and contraction of the air-hydrocarbon mixture above the liquid surface in a fixed-roof tank. The equation for these losses from crude oil given in API 2518 is:

$$L_y = K_c \left(\frac{24}{1000}\right)\left(\frac{P}{14.7-P}\right)^{.68} D^{1.73} H^{.51} T^{.50} F_P C$$

Where:

L_y = Breathing loss (bbls./yr.)

K_c = Factor to adjust gasoline breathing loss equation to breathing loss of crude oil = 0.58

P = True vapor pressure at bulk liquid temperature (psia)

D = Tank diameter (ft.)

H = Average outage including correction for roof volume (ft.)

T = Average daily ambient temperature change (°F)

F_p = Paint factor

C = Adjustment factor for small diameter tanks

The adjustment factor for small diameter tanks applies to those with diameters less than 30 ft. A curve giving these adjustment factors is to be found in API 2518.

Working losses are those associated with the displacement of vapors by liquid during tank filling. The API equation for crude oil working losses is:

$$F = \frac{2.25\ PV}{10{,}000} K_T$$

Where:

F = Working loss (bbls.)

P = True vapor pressure at bulk liquid temperature (psia)

V = Volume of liquid pumped into tank (bbls.)

K_T = Turnover factor (from equation (5) or Figure 11 in API 2518)

The equations given above for breathing and working losses can obviously be adjusted to other reporting terms, e.g. Mg/yr., lb./day, lb./1000 gals. throughput (working loss), using liquid densities, etc.

Recent studies have indicated that breathing losses from fixed-roof tanks are overestimated by a factor of four using the API 2518 equation[2,5,6]. Consequently, TRW, in its source category survey report on onshore production[1], discounted breathing losses by a factor of four in estimating per tank losses for the model tank battery. There is also an indication that working losses can be overestimated, particularly in the case of continuous service[2]. In the case of boiling or flashing crudes, the working losses can be underestimated. In summary, the predictive equations for breathing losses (as adjusted) and working losses are probably adequate for overall emission inventory preparation, but are subject to considerable error when used for individual tanks. Additionally, these predictive equations were not intended for use for onshore production tanks.

CONTROL TECHNOLOGY

Control technology for petroleum storage tanks at refineries, pipeline and marine terminals, and bulk plants is well known. As compared to uncontrolled fixed-roof tanks, emission reductions can be obtained with external floating-roof tanks, internal floating-roof tanks, and various types of vapor recovery systems. In general, regulations do not require controls for liquid petroleum storage where the true vapor pressure does not exceed 1.5 psig. Stabilized crudes have vapor pressures ranging from well under to well over this figure.

There are a number of differences between oil and gas production tanks at those refineries and terminals which impact the applicability of control technology. Some of these have been mentioned previously but will be summarized below:

- Oil and gas field tanks are generally much smaller than those at refineries and terminals.
- Tank batteries may be in remote areas without commercial electric power.
- Some oil fields do not have access to gas distribution systems to handle small amounts of gas produced with the oil.
- Gases evolved from unstabilized crude may contain CO_2 and H_2S.
- Tanks may be few in number and isolated by distance in production fields.
- Tanks in continuous service in production fields may have relatively small changes in liquid level associated with throughput.
- Production tanks may contain unstabilized or flashing crudes.

Taking into account the special circumstances of production tanks, two major options exist for VOC emission control: (1) vapor recovery and/or control, and (2) floating-roofs.

Emissions from fixed-roof tanks can be reduced by collecting and either recovering or combusting them. In a typical vapor recovery system, vapors remain in the tank vapor space until a pressure is reached which actuates the recovery system. The vapors are then collected by blowers or compressors and moved to the ultimate disposal system. Where natural gas is recovered, the tank vapor mixture can be transferred to the gas sweetening system (if any) or the natural gas liquids plant. An alternate means of disposal is a flare or fume incinerator (thermal oxidizer system). Such a system should have means of ignition, controlling combustion air, and preventing flashback to the tank vapor space. Where an open flare is used, it must be located in accordance with usual flare safety practices. Vapor recovery systems can be operated at efficiencies above 95 percent.

Floating-roof tanks reduce VOC emissions as compared to uncontrolled fixed-roof tanks by virtue of the fact that the floating-roof rises and falls with the liquid level during filling and withdrawal of the stored liquid and by reduction of the vapor space volume. Performance of floating-roofs is influenced by the effectiveness of seal design in minimizing gaps between the seal and the tank shell which result in direct exposure of liquid surface to the air.

Tanks with external floating-roofs have no fixed covers. A great variety of roof and seal designs have been used. All must provide for roof stability, precipitation drainage, gaging and inspection, roof support when the tank is empty, and effective perimeter sealing. Double seals have been shown to be very effective in reducing emissions as compared to single seals. In general, external floating-roof tanks are relatively large and field-erected and may be unavailable in the size range of most existing production storage tanks.

An internal floating-roof tank is essentially a fixed-roof tank with an internal cover floating on the liquid surface (contact cover) or suspended several inches above the surface with a perimeter pontoon (non-contact cover). Both aluminum and steel pans and aluminum sandwich (honeycomb) type covers are in use. Tanks can be retrofitted with internal covers. Internal covers offer several advantages over external covers for emissions reduction. They are not as susceptible to wind influenced losses and provide additional protection against solar radiant heating of the liquid surface. Additionally, they eliminate the need for precipitation drainage. Regular inspection to check for roof condition such as tilting or sinking is necessary. The space between the floating cover and fixed-roof must be ventilated to avoid build-up of VOC emissions to the lower flammable limit.

Emissions from floating-roof tanks, whether external or internal, are classified as "standing" and "wetting" (withdrawal). Standing losses result from gaps between the seal and the tank shell. As a result, some liquid surface is exposed to the atmosphere. When wind creates pressure differences above the floating-roof, air flows into the annular vapor space at locations of high pressure and an air-vapor mixture flows out at low pressure points. Vapors can also escape from open hatches or other openings, glands, valves, and fittings.

Wetting is another source of emissions from floating-roof tanks. Wetting loss is the vaporization of liquid from a wetted tank wall when a floating-roof is lowered by withdrawal of liquid. TRW has estimated the annual emissions from various controlled and uncontrolled tanks1). Table 9-2 shows these losses using a tank of 75,000 liter capacity in their model tank battery. These figures may be used for comparison purposes. Costs of these controls from the same study are given in Table 9-3.

Based upon the figures in Tables 9-2 and 9-3, the vapor recovery system is the most cost effective (lowest cost/amount controlled). It should be kept in mind that these are capital, not annualized costs. No credit for hydrocarbon recovery can be assigned in this case.

TABLE 9-2

CRUDE OIL STORAGE TANK UNCONTROLLED AND CONTROLLED VOC EMISSIONS

Device	Emission (Mg/yr.)
Uncontrolled fixed-roof tank	1.25
Non-contact internal floating-roof	0.8
External floating-roof tank (primary seals only)	0.63
External floating-roof tank (secondary seals)	0.19
Contact internal floating-roof tank	0.13
Vapor control system	0.05

TABLE 9-3

CRUDE OIL STORAGE TANK CONTROL COSTS

Control Technique	Cost per tank[a]	Cost per facility[b]
Vapor control	NA[c]	$13,000
Non-contact internal floating-roof	5,300	10,600
Contact internal floating-roof	6,300	12,600

a) Based on 79,500 liter welded storage tank; 1979 dollars.
b) Based on two tanks per facility; 1979 dollars.
c) NA = Not Applicable.

STATUS OF REGULATORY ACTIVITIES

The U.S. EPA has not regulated oil and gas production storage tanks as of the present time. The agency is conducting studies to determine whether air pollution sources within the category -- onshore production of crude oil and gas -- should be regulated with standards of performance promulgated under the authority of the Clean Air Act as amended August 7, 1977. Emissions of VOC from tank batteries are being considered under this study. Emissions from petroleum storage vessels over 40,000 gallons in capacity are regualated under 40 CFR, Part 60, Subparts K and Ka, but the regulation does not apply to storage vessels for petroleum or condensate at drilling or production facilities prior to custody transfer.

In general, state regulations are similar to Subparts K and Ka in that crude oil storage upstream of custody transfer from production facilities is exempted from the regulations. The California Air Resources Board is considering a model rule for onshore production of oil and gas but technical studies related to such a rule are still under way.

The Ventura County Air Pollution Control District in California has adopted applicable regulations under their Rule 71.1, Crude Oil Production and Separation. This rule, which is attached, requires that crude oil storage tanks in the tank battery, including wash tanks, be equipped with a closed-type vapor recovery system or equivalent.

REFERENCES

1. "Source Category Survey Report Onshore Production," prepared by TRW, Inc., Environmental Engineering Division for U.S. EPA, Economic Analysis Branch, RTP, NC, March 19, 1980.

2. "Hydrocarbon Emissions from Fixed-Roof Petroleum Tanks," prepared by Engineering-Science, Inc. for Western Oil and Gas Association, July 1977.

3. API Bulletin 2518, "Evaporation Loss from Fixed-Roof Tanks," Washington, D.C., 1962.

4. "Compilation of Air Pollution Emission Factors," U.S. EPA, Report No. AP-42, RTP, NC, August 1977.

5. "Emission Test Report - Breathing Loss Emissions from Fixed-Roof Petrochemical Storage Tanks," U.S. EPA, EMB Report No. 78-OCM-5, RPT, NC, February 1979, p. 173.

6. "Measurement and Determination of Hydrocarbon Emissions in the Course of Storage and Transfer in Above-Ground Fixed Cover Tanks With and Without Floating Covers," German Society for Petroleum Science and Carbon Chemistry (DGMK) and the Federal Ministry of the Interior (BMI), BMI-DGMK Joint Projects 4590-10 and 4590-11, translated for EPA by Literature Research Company, Annandale, Virginia.

APPENDIX

Ventura County Air Pollution Control District
State of California

Rule 71. Crude Oil and Organic Liquids
(Adopted June 20, 1978; Revised March 17, 1979, July 10, 1979

Rule 71. Crude Oil and Organic Liquids (Adopted 6/20/78; Revised 3/17/79, 7/10/79)

A. Applicability

1. The provisions of this rule shall apply to the production, gathering, separation and processing of crude oil and natural gas and the storage and transfer of crude oil and organic liquids excluding gasoline.

B. Definitions

1. For the purpose of this rule, a "closed-type vapor recovery system" means any organic vapor control system which is designed not to release or vent any organic gases to the atmosphere under normal operating conditions.

2. For the purpose of this rule, "vapor loss control efficiency" means a comparison of controlled emissions to those emissions which would occur from a fixed or cone roof tank in the same product service without a vapor control system. Base line emissions shall be calculated by using the criteria outlined in American Petroleum Institute Bulletin 2518.

3. For the purpose of this rule, "petroleum production permit unit" means any aggregation of equipment used exclusively for the production, gathering and separation of crude oil and natural gas which is included on a single Permit-to-Operate issued by the Air Pollution Control Officer.

4. For the purpose of this rule, "custody transfer" means the transfer of produced oil and/or condensate, after separation and/or treating in producing operations, from storage tanks or automatic transfer facilities to pipelines or any other forms of transportation.

5. For the purpose of this rule, "tank battery" means any tank, or any aggregation of tanks, used for the purpose of storing or holding crude oil or for the purpose of separating crude oil, water and/or natural gas. An aggregation of tanks will be considered a tank battery only if the tanks are located so that no one tank is more than 150 feet from all other tanks.

6. For the purpose of this rule, "wash tank" means any tank used for the purpose of the primary separation of crude oil and produced water.

7. For the purpose of this rule, "gauging tank" means any tank used exclusively for the purpose of measuring the production rate of crude oil from any petroleum production well.

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C. Severability

1. If any portion of this rule shall be found to be unenforceable, such finding shall have no effect on the enforceability of the remaining portions of the rule, which shall continue to be in full force and effect.

Rule 71.1 Crude Oil Production and Separation

A. Applicability

1. The provisions of this section of this rule shall apply to equipment used in conjunction with the producing, gathering and separation of crude oil and natural gas from any petroleum production permit unit prior to custody transfer.

B. Storage Tanks

1. No person shall place, hold or store any crude oil in any tank battery, unless all crude oil storage tanks in the tank battery, including wash tanks, are equipped with a closed-type vapor recovery system, properly installed, maintained and operated; or any other control technology considered by the Air Pollution Control Officer to represent the best available air pollution control technology at the time of installation. Any tank gauging or sampling device on a tank vented to a vapor control system shall be equipped with a gas-tight cover which shall be closed at all times except during gauging and sampling.

2. The provisions of subsection B.1 of this Rule shall not apply to any of the following:

    a. Any tank battery, including wash tanks, installed prior to June 20, 1978 for the purpose of holding and storing crude oil, having a true vapor pressure of less than 1.5 psi absolute;

    b. Any tank battery, including wash tanks, when it has been demonstrated to the satisfaction of the Air Pollution Control Officer that the cost of installing air pollution control technology is economically prohibitive and substantially exceeds the average cost per unit mass of air contaminant for all other stationary source controls. In making this determination:

        (i) Consideration shall be given to alternatives other than continued use of a tank battery or construction of a new tank battery including transfer by pipeline or other acceptable methods to an existing tank battery with appropriate air pollution control equipment; and

(ii) The cost of controlling a tank battery shall be averaged with the total cost of air pollution control for the entire stationary source;

c. Any crude oil production gauging tanks having a nominal capacity of 500 barrels or less;

d. Any tank battery, including wash tanks, holding or storing crude oil from any new crude oil production well, for a period of ninety days following initial production from that well.

3. Any person wishing to come under the provisions of subsection B.2.a. of this rule shall keep records to substantiate the applicability of that subsection. Such records shall include, for any crude oil, the true vapor pressure under actual storage conditions and the monthly throughput of the subject tank battery. These records shall be made available to the Air Pollution Control Officer on request. The true vapor pressure in psi absolute of stored liquid may be determined by using the nomographs contained in American Petroleum Institute Bulletin 2518 or by any other method approved by the Air Pollution Control Officer for determination of true vapor pressure.

C. Fugitive Emissions (Revised 11/20/79)

1. Any produced gas shall be routed to a vapor recovery system, flared, or controlled in some other manner considered by the Air Pollution Control Officer to represent best available control technology. The provisions of this subsection shall not apply in the following situations:

   a. During routine maintenance of any well, or

   b. During the first two weeks of production of an exploratory well, if the composition of the gas being produced is unknown (i.e., new reservoir) and there are no existing gas handling systems in the general vicinity.

2. All equipment used in conjunction with the production, gathering and separation of crude oil and natural gas from any petroleum production lease shall be routinely maintained in a manner representative of good oil industry practices so as to minimize air contaminant emissions.

D. Effective Dates

1. Any person owning or operating any existing equipment which requires modification to comply with the provisions of subsection B of this rule shall comply with the following schedule of increments of progress:

Tank Battery Throughput BBL/Month	Increment a	Increment b	Increment c	Final Compliance
5001 & Above	9-1-78	12-1-78	1-1-79	9-1-79
4001-5000	6-1-79	9-1-79	10-1-79	6-1-80
3001-4000	6-1-80	9-1-80	10-1-80	6-1-81
2001-3000	6-1-81	9-1-81	10-1-81	6-1-82

Revised 3/29/79

SECTION 10

PETROLEUM COKING PROCESSES

PROCESSES AND EMISSIONS

Low value residual type oils are converted to higher value products through a thermal cracking process called coking. Thermal tars and vacuum residuals are cracked at high temperature and atmospheric pressure. The resulting products are petroleum coke, gas oils and lighter petroleum stocks. Presently, delayed coking is the most widely used process1).

DELAYED COKING PROCESS AND EMISSIONS

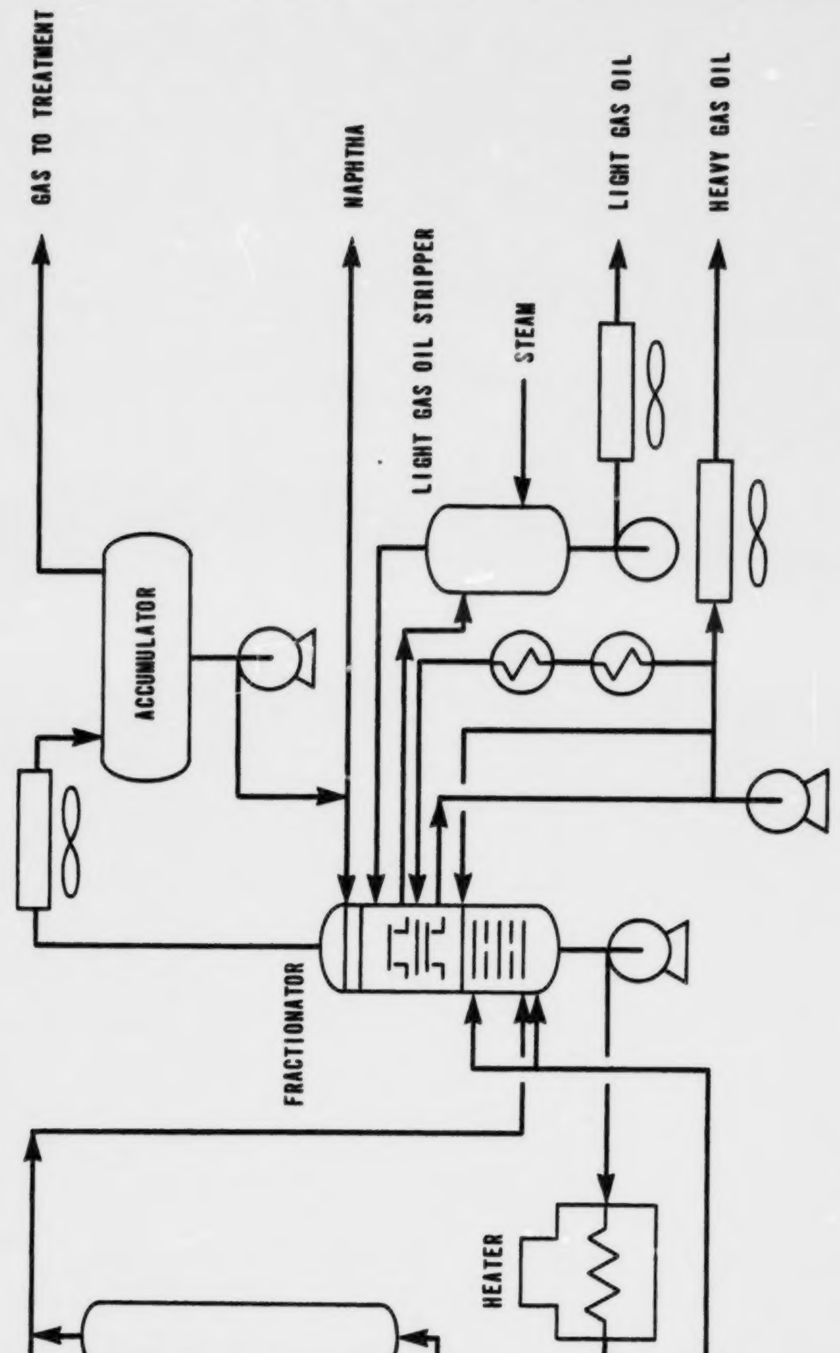
The heated charge stock is fed into the bottom of the fractionator, here the light ends are stripped off. The recycle from the coke drum is combined with the remaining feed and is quickly heated in the coking heater to 480-590°C (900-1100°F). The heating rate is controlled by steam injection. In the coke drum, the vapor-liquid from the heater is converted to coke under the proper conditions of residence time, pressure, and temperature. The thermal cracking products are recovered in the fractionator once the vapors from the top of the drum have returned. Once the onstream coke drum is filled to the proper capacity with coke, it is taken offstream and is quenched/purged with steam. When the temperature reaches the desired level, the drum is opened and the coke is cut with high pressure water.

PROCESS EMISSIONS AND EMISSION POINTS

Considerable quantities of steam and hydrocarbons may be released to the atmosphere when the coke drum is opened. The cutting operation may also emit hydrocarbons when more steam is produced by vaporization of the cutting water. Also, the cutting itself may release pockets of trapped steam and hydrocarbons. Some of the hydrocarbons released can include polynuclear aromatics and other hazardous compounds since the coker conditions favor their production. See the following Figure 10-1 for flow chart of delayed coking process.

FIGURE 10-1

DELAYED COKING PROCESS


GAS TO TREATMENT
NAPHTHA
LIGHT GAS OIL STRIPPER
STEAM
LIGHT GAS OIL
HEAVY GAS OIL
ACCUMULATOR
FRACTIONATOR
HEATER
COKE DRUMS
FEED START

REFERENCE NO. 3

CONTROL TECHNOLOGY

Venting the quenching stream to a vapor recovery or blowdown system would lessen the hydrocarbon emissions from coking processes. When the drum cools to 100°C (212°F), the steam purge can be replaced by a water flood. Additional cooling to nearly ambient temperature will reduce steam and hydrocarbon vaporization and subsequent escape when the drum is opened[1].

STATUS OF REGULATORY ACTIVITIES

The state and local agency regulations concerning the petroleum industry do not include specific rules addressing coking. In general, the regulations are stated in a blanket fashion, and worded as "those processes involved in the production of gasoline, kerosene, distillate and residual fuels, or other products through distillation, cracking, extraction, or reforming of petroleum derivatives, must control the emissions from vacuum producing systems, wastewater separators, and process unit turnarounds using the methods specified.... ". The rules also specify the storage, loading and unloading of petroleum products and the required controls and precautions.

The State of the Illinois air laws regarding organic discharge to the atmosphere do indicate the following: ".....any petroleum fluid coker; or any other waste gas stream from any petroleum or petrochemical manufacturing process; in excess of 100 ppm equivalent methane (molecular weight of 16.0).

REFERENCES

1. Control Techniques for Volatile Organic Emissions from Stationary Sources, EPA-450/2-78-022, May 1978.

2. Nelson, W. L., Petroleum Refinery Engineering. McGraw-Hill, Fourth Edition, 1969.

3. Hydrocarbon Processing, Page 154, September 1980.

SECTION 11

PLASTIC PARTS PAINTING

PROCESSES AND EMISSIONS

A wide variety of industries produce plastic products which are painted. There are other methods of imparting color to a plastic product, such as use of pigmented molding compounds and use of colored gel coats in fiberglass reinforced resin products, but these techniques are not covered here. Both complete assemblies and component parts are included in those items painted. In the latter case, painting is often utilized to obtain close color matching with other parts. Some of the plastic parts categories where painting is used are instrument knobs, radio grilles, automobile dashboard parts and body filler panels, sporting goods, cosmetic cases, control panels and nameplates for appliances, furniture parts, toys, lamp housings, canisters, clock bezels, and office equipment parts.

No comprehensive emission information for plastic parts painting by source category was readily available for use in this report, and no direct survey was attempted. Indirect information was obtained indicating that VOC emissions from plastic parts painting at some automotive parts suppliers were in the range of 1000 tons per year. Both primers and topcoats are applied using solvent-based coatings containing solvents such as xylene, naphtha, diisobutylketone, and methylethylketone. Solvent content of coatings ranged from 62 to 79 percent by weight. Some automated electrostatic coating lines were utilized. An approximate paint transfer efficiency of 55 percent was estimated for electrostatic painting.

Most plastic parts are relatively small and are painted with spray techniques. These include compressed air, airless, and electrostatic methods of application. Coatings used are somewhat more limited as compared to metal products because the organic substrate limits coating compatibility and the temperature of curing. Nevertheless, the solvent content of paints used for plastic parts is not unlike that of coatings used on miscellaneous metal products. In the Control Techniques Guidelines (CTG) document for this latter category, enamels (at about 30 to 40 volume percent solids) and lacquers (at about 10 to 20 percent solids) were listed as being commonly used.1)

CONTROL TECHNOLOGY

At the present time the most applicable process related control techniques for reducing VOC emissions from plastic parts painting are:

1) Use of higher solids coatings;

2) Use of radiation-cured coatings; and

3) Use of higher transfer efficiency coating methods such as electrostatic and airless spraying.

In the case of higher solids content coatings, there is a general development in this direction in the entire coatings field. To the extent that such coatings are compatible with plastic substrates, they could be adapted for use with plastic parts.

Kut in Chapman and Anderson2) discusses the use of radiation-cured coatings for plastic automobile radiator grilles and instrument panels. Advantages claimed include rapid curing at low temperatures, minimal pollution because of the use of "solvent free" coatings, high throughput rates, and less floor space requirements as compared to thermal polymerization techniques. The term "solvent free" coatings refers to those in which liquid hydrocarbons such as styrene impart fluidity during painting, but which are polymerized during the radiation cure to become part of the coatings. Some losses of these compounds do occur prior to curing. A large capital expenditure is required for radiation cure equipment.

Techniques to obtain higher transfer efficiencies are potentially capable of achieving significant reductions in VOC emissions. Both electrostatic and airless (hydraulic) spraying techniques can result in higher transfer efficiencies (ratio of coating reaching object to be coated to that consumed). In the case of spray application methods, the excess coating is lost in overspray and bounceback.

The conventional method for applying surface coatings to many plastic parts is with an air atomizing spray gun. Transfer efficiency with these systems is generally less than 50 percent.

Electrostatic coating is based on the principle that opposite electrical charges attract each other. The atomized coating particles are negatively charged by the application device and the article to be coated is positively charged or grounded. Transfer efficiencies with hand-held equipment can typically be improved to 65 percent, and under optimal conditions, using automated bell and disc systems with conveyorized parts, efficiencies can reach 85 to 95 percent.3) Because plastic is non-conductive, it must be treated with a sensitizing material. Plastic products which have been successfully coated using electrostatic techniques include containers, golf balls, grill work, automotive grilles and instrument panels, picture frames, women's shoe heels, and toilet seats.

Airless spraying utilizes hydraulic pressure in lieu of air pressure to atomize the coating. While coating particles are not attracted to the target such as in electrostatic spraying, there is a reduction bounceback and in coating material which follows airstream lines instead of impacting the target.

Add-on controls such as incineration or activated carbon adsorption are equally as applicable to plastic parts painting as to many other surface coating categories. A discussion of these techniques, which for the most part is applicable to plastic parts painting, can be found in the CTG for Miscellaneous Metal Parts and Products1) and in a general EPA Guideline for Control Methods for Surface Coating Operations4).

STATUS OF REGULATORY ACTIVITIES

Many states and local agencies have general rules which limit emissions of volatile organic compounds from industrial processes and surface coating operations. These rules are generally expressed in terms of mass limits per unit of time. Rule 442 of the South Coast Air Quality Management District, California; and Rule 2, "Miscellaneous Operations" and Rule 4, "General Solvent and Surface Coating Operations", Bay Area Air Quality Management District, California are examples of such rules. No rules specifically directed towards painting of plastic parts were found to exist.

REFERENCES

1. "Control of Volatile Organic Emissions from Existing Stationary Sources - Volume VI: Surface Coating of Miscellaneous Metal Parts and Products," EPA-450/2-78-015, U.S. EPA, OAQPS, RTP, NC 27711, June 1978.

2. B. N. Chapman and J. C. Anderson, Science and Technology of Surface Coatings, Academic Press, New York and London, 1974.

3. "Electrostatic -- A Dark Horse in Finishing Alternatives," Wood and Wood Products, February 1980, p. 25.

4. "Control of Volatile Organic Emissions from Existing Stationary Sources - Volume I: Control Methods for Surface Coating Operations," EPA-450/2-76-028, U.S. EPA, OAQPS, November 1976.

SECTION 12

RAILROAD TANK CAR LOADING OF VOLATILE ORGANIC LIQUIDS

This section reviews the loading of volatile organic liquids (VOL's) into railroad tank cars. Emissions generated in these loading operations and suitable techniques for the control of these emissions are discussed and cost effectiveness calculations for a typical VOL are presented. Existing air pollution regulations covering railroad tank car loading of VOL's are reviewed.

PROCESSES AND EMISSIONS

The loading of volatile organic liquids into railroad tank cars takes place nationwide at railroad tank car loading terminals serving chemical plants and petroleum refineries, and at pipeline, marine and independent (toll) terminals.

There were approximately 200,000 railroad tank cars in service in 1979, about 98 1/2% of which were owned by shippers and private railcar companies such as General American Transportation Corp. (GATX), North American Car Corporation, etc. Each of these cars was, on the average, loaded and shipped about 10 times during 1979[1)].

The 1979 aggregate volume of diverse (organic and inorganic) chemical and petroleum products shipped by tank car was approximately 45 billion gallons. Petroleum products account for about 18% of the total, with volume of tank car shipments tending to decline in recent years. Volume of tank car shipments of all chemical products represents 82% of the total and has tended to grow in recent years, increasing about 3.5% from 1978 to 1979[1)].

Only those VOL's falling within a vapor pressure range of 0.5 to 13 psia @ 60°F were considered in assessing the significance of tank car loading of chemical and petroleum products as a source of volatile organic compound emissions (VOC's). VOL's with vapor pressures below 0.5 psia @

60°F produce a relatively insignificant quantity of emissions when loaded into tank cars, even under the worse loading conditions. VOL's with vapor pressures above 13 psia @ 60°F (which are in most cases liquified gases) are always loaded under pressure sealed, vapor controlled conditions by venting the tank car vapor space to the vapor space of the storage vessel from which the VOL is drawn (termed vapor balance). While this is done primarily to conserve valuable product, it effectively eliminates VOC emissions to the atmosphere during the loading operation.

Within the vapor pressure range of 0.5 to 13 psia @ 60°F fall about 4.5 billion gallons of VOL's shipped by railroad tank car, about 10% of the total annual shipments of chemical and petroleum products during 1978 and 1979.

Table 12-1 summarizes the approximate volumes of the 10 VOL's loaded and shipped in railroad tank cars in largest quantities in 1978[2)].

The volume of tank car shipments of these ten chemicals accounted in 1978 for 80% of the total volume of all VOL's shipped. Crude oil, gasoline and associated petroleum products such as naptha and hexane comprise well over one half of all the VOL's with vapor pressures between 0.5 and 13 psia shipped by railcar in 1978[3)]. Based on information obtained in a survey of the railcar loading industry covering 33 terminals,[4] the average railcar loading terminal loads about 15 million gallons of VOL's/year (roughly 800 railcars/year), with range of throughput volume extending from about 1 million up to 50 million gallons/year. The average VOL loaded in these terminals has a vapor pressure of about 1.7 psia @ 60°F.

Description Of Equipment

Equipment used to load VOL's into railroad tankcars consists of loading arms and miscellaneous pumps, valves, meters, etc., generally mounted on a structure termed a loading rack, positioned within the railroad siding area designated as a railcar loading terminal.

Railroad Tank Cars. Railroad tank cars consist of cylindrical tanks mounted on appropriate underframes and wheeled trucks (Figure 12-1). Recently constructed tank cars are of welded or seamless construction,

TABLE 12-1

QUANTITIES OF TOP TEN VOL's LOADED IN RAILROAD TANK CARS 1978

VOL	MM GALLONS LOADED
CRUDE OIL	1162
ETHANOL	558
GASOLINE	555
NAPTHA	449
METHANOL	262
ACRYLONITRILE	202
PROPYLENE OXIDE	179
ACETONE	92
CYCLOHEXANE	79
HEXANE	61

with domed welded heads. Some tanks of older riveted construction are still in limited use. Materials of construction are primarily mild steel, stainless, or aluminum. Interiors of tanks may be lined with materials such as rubber or poly (vinyl chloride) suitable for specific service with various corrosive chemicals.

Various classes of tanks are insulated to retard heating or cooling of the tank contents during transit. Tanks may be equipped with interior steam coils to facilitate unloading by reducing the viscosity of the cargo, especially during cold weather5).

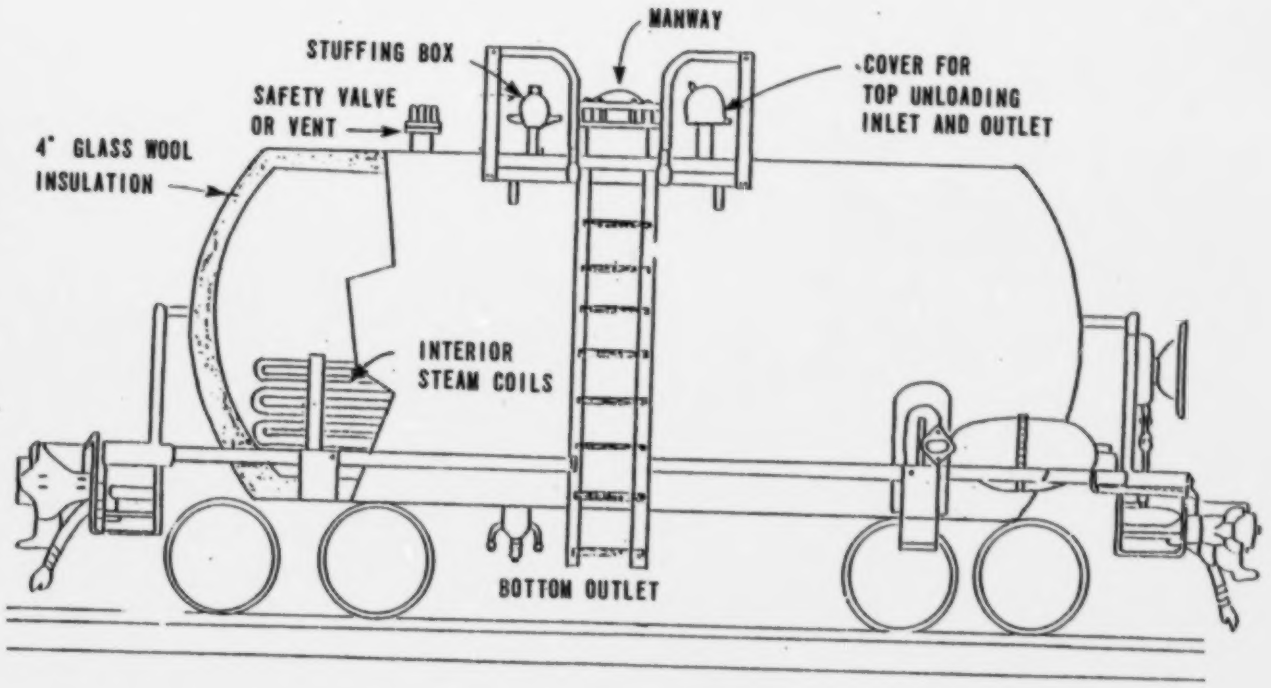
Structural requirements for railroad tank cars are generally covered in the Code of Federal Regulations by Title 49, Part 179, Subpart D. Part 179.202 encompasses regulations specific to particular chemicals. In addition, 49 CFR 172 presents regulations on classification and identification of hazardous materials, and specifies marking and placarding requirements for tank cars in which they are shipped.

VOL's are generally suitable for shipment in tank cars designated as general service tank cars. Such tank cars are designed to accomodate moderate interior pressures not in excess of 100 psig, and are generally equipped with over pressure relief valves set at 35 to 100 psig. Figure 12-1 shows such a general service tank car, with insulation and interior steam coils.

Tank cars are classified, tested and certified by U.S. Department of Transportation in cooperation with the Association of American Railroads (AAR). The general service classification appropriate for the shipment of VOL's encompasses DOT classes 103, 104 and 111. The full specification number (e.g., 111A60ALW) designates the class (111), a test pressure (60 psig), a material of construction (Aluminum), and a type of construction (welded).

Different sizes of tank cars are available within each classification. Common sizes within the general service classification are 8000, 10,000, 20,000 and 23,500 gallons. Also available for specialized service are various other sizes up to a maximum of 33,500 gallons. Maximum size is restricted by allowable maximum total weight of tank car

GENERAL SERVICE RAILROAD TANK CAR


MANWAY
STUFFING BOX
COVER FOR TOP UNLOADING INLET AND OUTLET
SAFETY VALVE OR VENT
4" GLASS WOOL INSULATION
INTERIOR STEAM COILS
BOTTOM OUTLET

and cargo, particularly if the shipment is to qualify for unrestricted movement among the various railroad lines[5]).

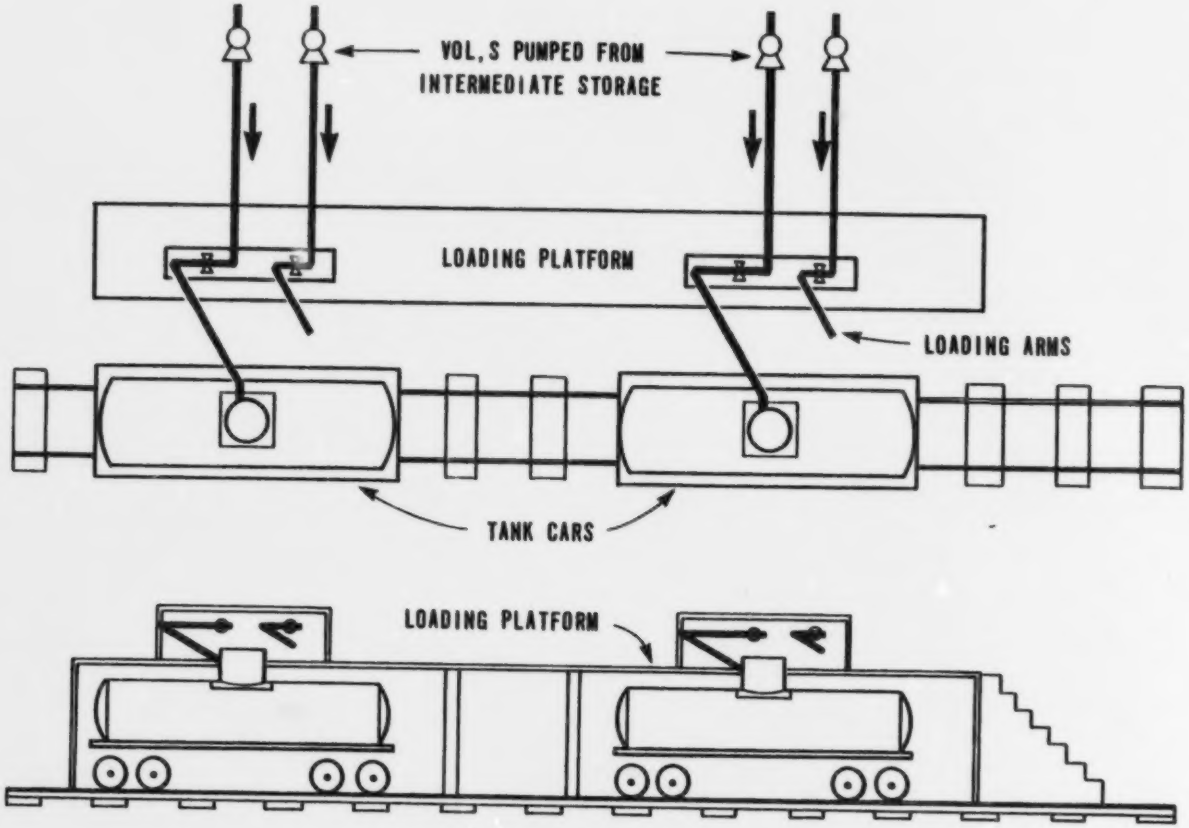
Various loading and unloading arrangements are provided on the types of tanks within the general service railroad tank car classification. For loading, all tank cars within the general service classification are provided with a hatch (manway) of various diameters through which the loading device (arm) may be inserted. For unloading, all general service tank cars are equipped with a bottom unloading valve positioned directly under the tank. This valve may be operated from the top of the tankcar by a valve extension handle. Many tank cars of modern construction have been fitted with a top unloading piping arrangement comprising an inlet for pressurized inert gas and an outlet pipe extending from the top unloading port approximately to the bottom of the tank. The cargo is forced by gas pressure from the tank through the outlet pipe, and is discharged at the top of the tank.

Railroad Tank Car Loading Terminal. A railroad tank car loading terminal is broadly considered to be the general area within which are located the railroad siding(s), structures (loading rack), and equipment necessary to load liquids into tank cars.

Within a tank car loading terminal may be one or more loading racks. The loading rack is generally a raised platform positioned adjacent to the railcar siding and includes the loading arm(s), piping, valves, pumps, meters and other equipment necessary to the loading process. The working area of the rack is elevated to the approximate level of the loading hatch of the tank car positioned on the siding. Most loading racks have a number of tank car loading stations, and, as a result, frequently load a number of tank cars simultaneously. The rack structure may include a roof covering the tank car stations on the siding. Individual racks within a terminal are generally designed to accomodate loading of specific classes of materials. Much of the equipment associated with the rack is dictated by the properties of the class of materials intended to be loaded. A terminal may contain one or more of these racks, and may be as simple as a single rack accommodating a single arm or multiple arms, or as complex as two or more racks with multiple arms. Figure 12-2 shows a simple terminal comprising a single siding and positions for 2 railcars.

FIGURE 12-2

SMALL RAILROAD TANK CAR LOADING TERMINAL


VOL,S PUMPED FROM
INTERMEDIATE STORAGE
LOADING PLATFORM
LOADING ARMS
TANK CARS
LOADING PLATFORM

Loading Arm. The loading arm is the extension of the piping which carries the VOL from intermediate storage to the tank car.

For liquids of relatively low volatility, this extension may consist of a large diameter flexible hose fitted with an angled pipe which can be inserted into the open tank car hatch. The angled pipe may vary in length from a few feet to a length long enough to reach to the bottom of the railcar tank. In place of the flexible hose, the arm may be constructed completely of pipe and fitted with double swivel joints to permit positioning of the pipe into the tank car.

A third type of loading arm in general use for the loading of highly volatile liquids and compressed gases is also adaptable for the loading of VOL's in general. This loading arm terminates in a union or coupling to permit connection to existing piping leading through the railcar dome and extending approximately to the bottom of the tank. In conjunction with this type of loading arm, a vapor return line is installed to return vapors vented from the tank car to vapor collection ducting or piping along the rack. Since loading of VOL's with this type of loading arm takes place with the hatch closed and sealed, a sensing device such as a magnetically activated float within the tank is frequently used to monitor liquid level within the the tank car.

Preparation of Railcars for Loading. Railroad tank cars are occasionally cleaned prior to loading. Most railroad tank cars however, are owned and leased by shippers, and are used exclusively and repeatedly for shipping a single chemical (dedicated service). These cars are only cleaned when testing or inspection reveals contamination. Tank cars owned or leased by shippers of petroleum products are considered to be in non-specific dedicated service. Since the types of products shipped in these cars are frequently not cross-contaminating to a serious degree, these cars are used to ship various essentially similar products without cleaning. These cars are only cleaned when inspection or sampling reveals contamination, or when the material to be loaded differs substantially from the material previously shipped.

Tank cars in non-dedicated service represent a relatively small proportion of the total cars in chemical service. Such cars are routinely cleaned between loadings unless sampling, testing and inspection can establish the compatibility of the VOL to be loaded with the residual liquid from the previous loading.

Tank cars are cleaned at either the shipping and receiving terminals or at railcar maintenance and repair facilities. The cars are cleaned with the use of a steam hose, pressure wand, or rotating spray heads placed through the manhole. The residual chemical and the cleaning solution are flushed from the tank with water. Although much of the VOL cleaned from the tank car will eventually be lost to the atmosphere, the quantity of emissions occurring as the result of cleaning of railroad tank cars is considered to be negligible.

Open Hatch Loading. Railroad tank cars are almost exclusively loaded from the top of the tank. The principal methods of loading tank cars are the splash loading method and the submerged fill pipe method. In the splash loading method the fill pipe dispensing the liquid is only partially lowered into the tank car. Significant turbulence and vapor-liquid contacting occurs during splash loading, resulting in high levels of vapor generation. If turbulence is high enough, entrainment of liquid droplets in the vapor may take place. In the submerged fill pipe method, the fill pipe descends almost to the bottom of the tank car. As a result, the fill pipe opening is below the liquid during the major portion of loading, resulting in a significant reduction in liquid turbulence and vapor-liquid contacting.

Both the splash loading and submerged fill loading methods are conducted at rates as low as 50 gallons/minute and as high as 400 gallons/minute, depending on the viscosity of the VOL being loaded, the available pressure and the piping sizes in the system. Accordingly, tank car filling times vary from as long as 8 hours for a 23,500 gallon tank car filled at the slowest practiced rate to as quickly as 1/2 hour for a 10,000 gallon tank car filled at the highest practiced rate.

Railroad tank cars are filled to slightly less than their nominal capacity, as prescribed by U.S. DOT regulations. The remaining unfilled volume, termed outage, is volume reserved for liquid expansion occurring as a result of increasing temperature. Maintenance of a vapor space within the tank also insures that vapor and not liquid is vented through the tank car pressure relief valve under transient conditions of excess temperature and pressure[5]).

Closed Hatch Loading. Because of the hazardous or highly volatile nature of some VOL's loaded into railroad tank cars, closed hatch loading techniques are also practiced. As described earlier, some general service tank cars have been fitted with a top unloading piping arrangement. This piping arrangement has been adapted for VOL loading through use of the unloading pipe for loading and the use of the pressurization port for collection of VOC emissions.

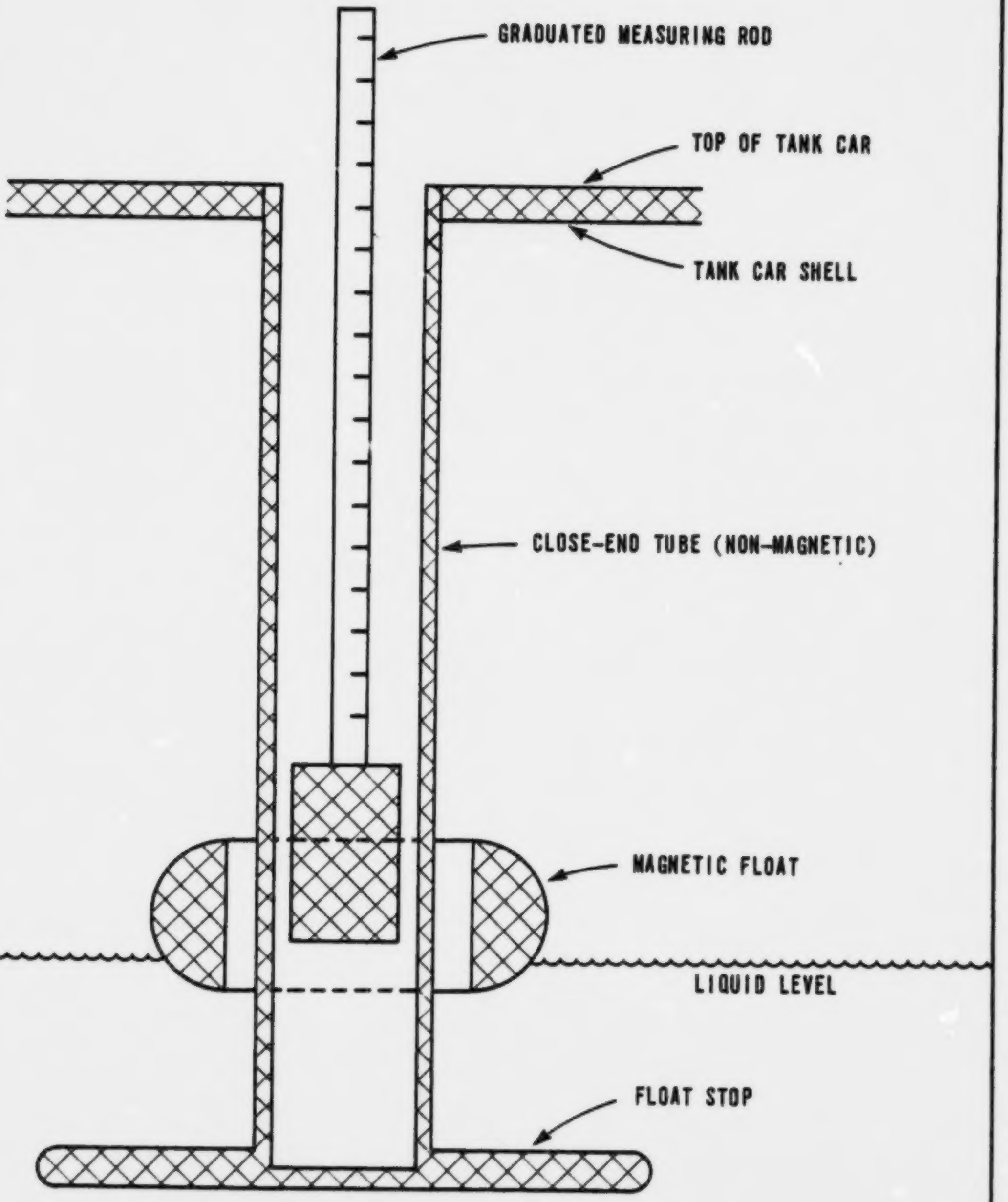
Since the number of general service tank cars fitted out with this top unloading piping arrangement is limited, railroad tank cars designed for liquified gas service are sometimes used for loading of hazardous VOL's or VOL's with high vapor pressures. These cars are of course specifically designed for sealed hatch loading.

Measurement of Liquid Level. Since loading must not proceed to full nominal tank capacity, liquid level measurement during loading is necessary. In splash and submerged fill loading, visual sighting of the liquid level and/or use of a graduated dip stick is a frequently used liquid level measuring technique. A type of level sensing device used in sealed hatch loading comprises a magnetic float surrounding a closed tube extending below the required final liquid level. The magnetic float, which rises with the rising VOL, actuates a corresponding magnet on the end of the measuring rod positioned within the closed end tube (Figure 12-3).

Sampling of VOL Cargo During Loading. Conventional industrial quality control practice requires sampling of the VOL loaded into the tank. Ideally, sampling is done in such a way that the sample is representative of the composite material in the tank. In splash loading or submerged fill loading samples are conveniently dipped from the tank through the open hatch as required. In closed hatch loading samples are taken at appropriate intervals through a valve in the piping to the loading arm.

Temperature Measurement of Loaded VOL. VOLs are loaded at a wide range of temperatures. Since density and volume vary with temperature, it is necessary for the shipper to measure the temperature of the VOL loaded and

MAGNETIC LIQUID LEVEL MEASURING DEVICE


GRADUATED MEASURING ROD
TOP OF TANK CAR
TANK CAR SHELL
CLOSE-END TUBE (NON-MAGNETIC)
MAGNETIC FLOAT
LIQUID LEVEL
FLOAT STOP

correct the volume of VOL from standard conditions in determining the outage required by USDOT regulations. Such temperature measurements are made either through the open hatch during splash or submerged fill loading, or, in the case of closed hatch loading, by inserting a thermometer through the thermometer well.

Unloading of VOL's. Since many VOL's are not chemically reactive with oxygen, air is vented or pressurized into the car during unloading. If such materials are chemically reactive with oxygen, an inert gas such as nitrogen is vented or pressurized to the tank while unloading.

Sources of Emissions

Emissions occur during the VOL loading of railroad tank cars as VOC's in the vapor space of the tank car are expelled from the tank by the rising level of the VOL being loaded. Residual VOC's from the previous unloading operation are present in the vapor space of the tank (unless the tank car was cleaned after unloading). In addition, VOC emissions are also produced during the loading operation through evaporation of the VOL being loaded. In the case of splash loading through the open hatch, some entrainment of VOL droplets takes place.

The following equation6) can be used to calculate an emission factor for a VOL loaded into a railroad tank car:

$$L_L = 12.46 \frac{SPM}{T}$$

where: L_L = Loading loss (lb/10^3 gal of liquid loaded)
M = Molecular weight of vapors (lb/lb-mole)
P = True vapor pressure of liquid loaded (psia)
T = Bulk temperature of liquid loaded (°R)
S = Saturation factor (see Table 2-1).
= 0.5 for submerged loading of a clean tank car
= 0.6 for submerged loading of a dedicated service tank car
= 1.45 for splash loading of either a clean or dedicated service tank car

Data on quantities of VOL's shipped during 1978 was obtained from the U.S. Department of Transportation Waybill Study2). This data was used with emission factors obtained from the above equation to calculate approximate total potential emissions for the continental United States for 1978. A saturation factor of 0.6 was used in the calculations as being typical of a reasonable "worst case" situation, although it is recognized that significant quantities of VOL's are loaded with some type of existing emission control.

On this basis, Table 12-2 presents the maximum potential emissions for the quantity of VOL's with vapor pressures between 0.5 and 13 psia loaded into railroad tank cars during 1978.

CONTROL TECHNOLOGY

This section discusses suitable methods currently practiced for the collection of VOC's emitted during the loading of VOL's into railroad tank cars, and presents effective techniques for the control of these VOC's.

Vapor Collection. Vapor collection is the physical collection of the VOC vapor expelled from the tank car during the loading of a VOL. Three vapor collection techniques are currently practiced within the railroad tank car loading industry:

- Collection by vapor balance, in which VOC emissions vented from the railcar tank are returned to the vapor space of the VOL storage vessel,
- Suction pipe collection in open hatch loading of VOL, in which the VOC emissions are collected at the open hatch with a suction pipe,
- Collection through the vent port, in which VOC emissions are collected directly from the vent port of the top unloading piping arrangement incorporated into many railcars.

A fourth technique, use of a hatch-sealing plug, is in common use for top loading of gasoline tank trucks. This technique is satisfactory in the gasoline truck loading industry because of the relatively few standard hatch diameters installed in gasoline tank trucks, and because gasoline tank trucks to be loaded at a bulk terminal are generally in captive use and accordingly are fitted with a specific hatch size to mate with the hatch sealing plug in use at that terminal. Railroad tank cars however, have been built with hatches of many different diameters. It would be impractical to have loading arms fitted with hatch sealing plugs of the diameters required to mate with each of the many railcar hatch diameters in the existing railcar fleet.

TABLE 12-2

TOTAL VOL TANK CAR LOADINGS AND EMISSIONS
1978

Gallons of VOL's loaded Millions	Maximum Potential VOC Emissions, Tons
4,908	5,300

Collection by Vapor Balance. VOLs with high vapor pressures (i.e., above 10 psia @ 60°F) are occasionally loaded into railroad tank cars designed for transport of liquified gases (Figure 12-4). The loading equipment of such cars is designed to permit sealed loading with measurement of outage and temperature while venting the vapor space of the tank car to the vapor space of the liquified gas storage tank (vapor balance).

Vapor balancing permits sealed hatch loading of high vapor pressure VOLs with no loss (other than leaks, spills etc.) of VOCs to the atmosphere. This loading technique is also frequently used in loading of flammable, toxic, or reactive chemicals, the vapors from which must be contained for reasons of health or safety.

Collection of VOCs During Open Hatch Loading of VOL. VOLs of moderate vapor pressure (i.e., up to 5 psia @ 60°F) are commonly loaded through the open hatch of railroad tank cars. Collection of VOCs expelled from the open tank car hatch is difficult. Occasionally, a flexible suction hose is positioned within the open hatch (Figure 12-5), and some collection of VOCs by this suction hose will take place. Collection efficiency of such a device is very poor, however, and, a significant portion of the expelled VOCs escape collection and are released to the atmosphere.

Collection of VOCs Through Top Unloading Piping. As noted earlier, many general service tank cars are fitted with a top unloading piping arrangement in which gas pressure is used to force the liquid to be unloaded out the unloading pipe which extends to the bottom of the tank car.

This piping arrangement has been adapted for VOL loading (Figure 12-6). The unloading pipe is used as a VOL loading pipe, and the gas pressurization port is used for VOC venting. As the VOL is loaded through the unloading pipe, the rising liquid level expels VOC vapors from the tank through the gas pressurization port, thereby collecting the VOC vapors for control.

VOC Vapor Conditioning

VOC vapor conditioning refers to the saturation of the vapor with additional VOC or the dilution of the vapor with air. The VOC vapor stream is saturated with additional VOC to increase the total VOC concentration

FIGURE 12-4

VAPOR BALANCE IN VOL LOADING INTO
LIQUIFIED GAS SERVICE TANK CAR

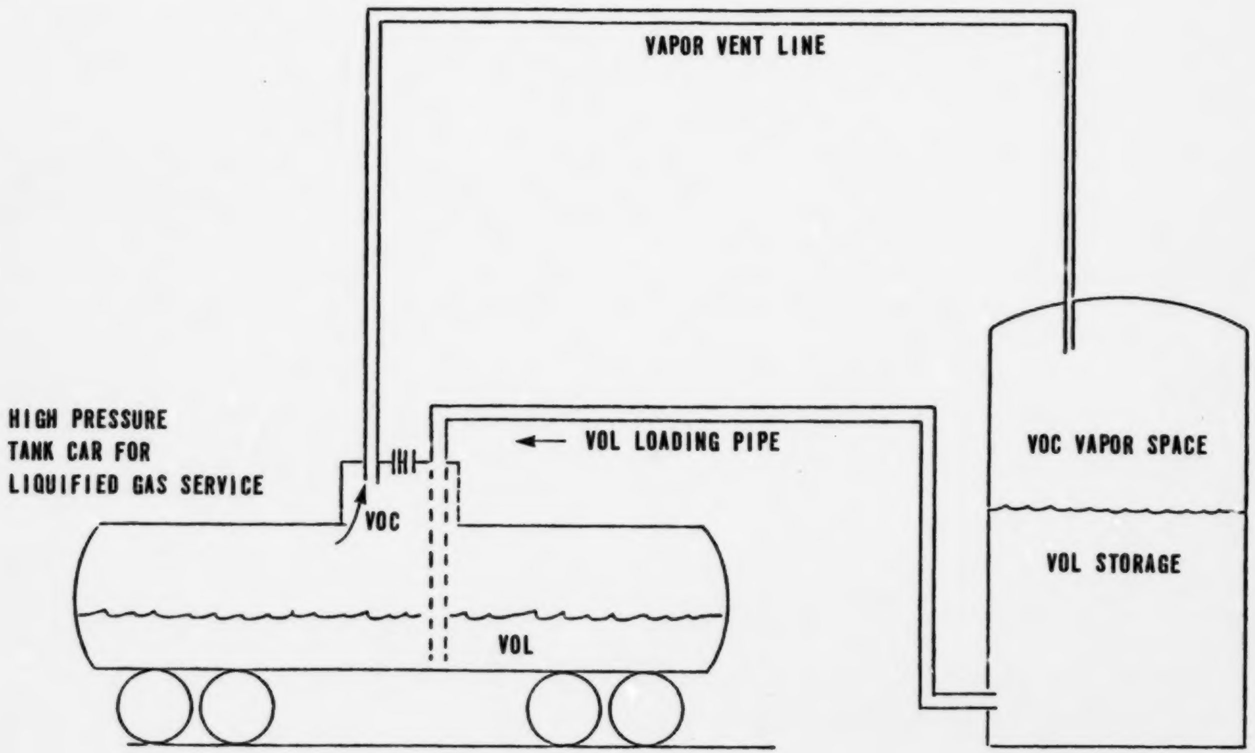

VAPOR VENT LINE
HIGH PRESSURE
TANK CAR FOR
LIQUIFIED GAS SERVICE
VOC
← VOL LOADING PIPE
VOL
VOC VAPOR SPACE
VOL STORAGE

FIGURE 12-5

VOC VAPOR COLLECTION BY SUCTION PIPE DURING
OPEN HATCH TANK CAR LOADING OF VOL,S

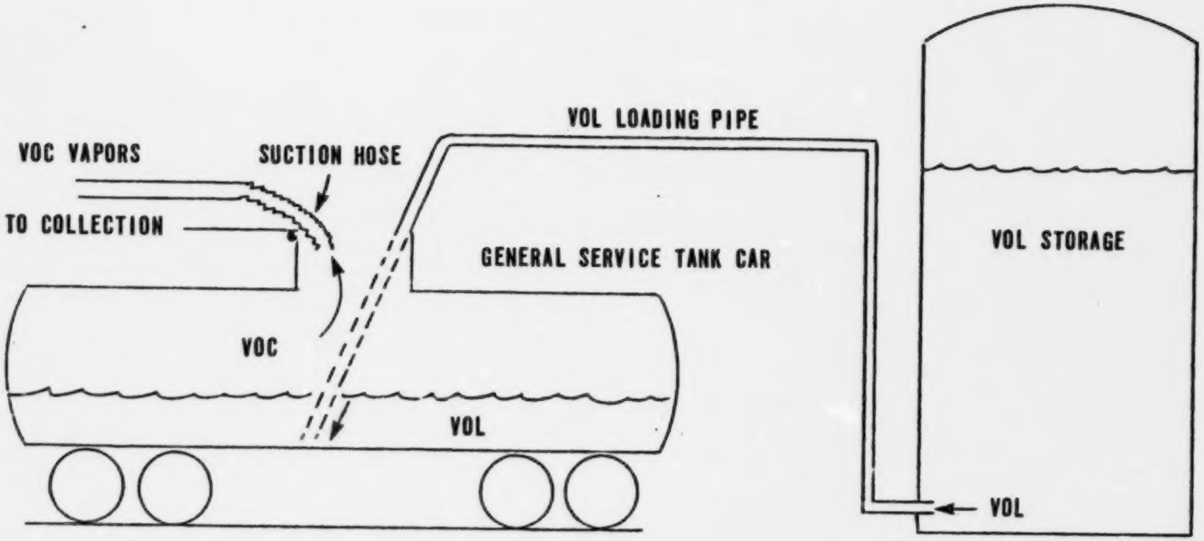
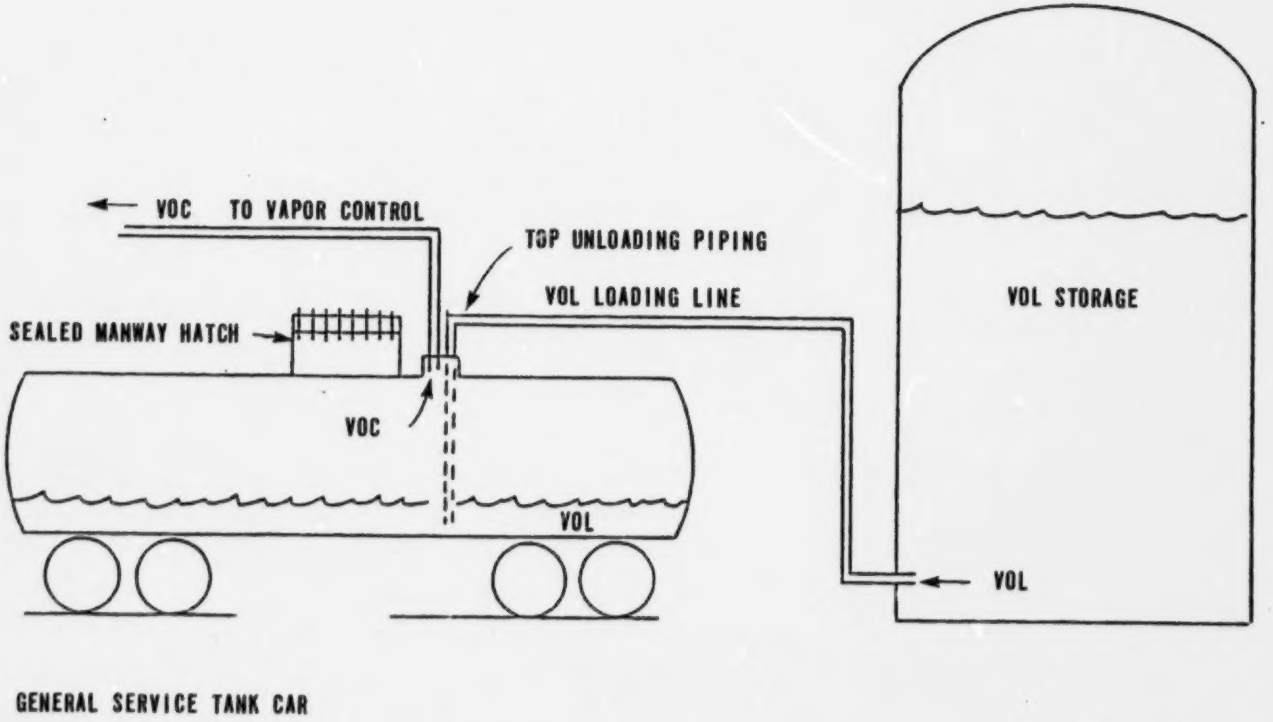

VOL LOADING PIPE
VOC VAPORS
SUCTION HOSE
TO COLLECTION
GENERAL SERVICE TANK CAR
VOL STORAGE
VOC
VOL
VOL

FIGURE 12-6

VOC VAPOR COLLECTION FROM TOP UNLOADING PIPING
OF GENERAL SERVICE TANK CAR


← VOC TO VAPOR CONTROL
TOP UNLOADING PIPING
VOL LOADING LINE
VOL STORAGE
SEALED MANWAY HATCH
VOC
VOL
← VOL
GENERAL SERVICE TANK CAR

to a level above the upper explosive limit (UEL), or is diluted with air to a level below the lower explosive limit (LEL). VOC vapor conditioning should occur as soon as possible after VOC collection, to avoid transport of a potentially explosive VOC stream.

In the loading of VOLs into railroad tank cars the composition of the expelled stream is influenced by the type of service the tank car is in, the prior unloading method, and whether cleaning is performed between unloading and loading.

Not all vapor streams collected from tank cars would require conditioning. In those cases where the tank car is in dedicated service and has not been cleaned following its last unloading, the VOC concentration in the vapor space within the tank car is frequently, but not always, above the UEL.

Tank cars which were top unloaded under nitrogen pressure will contain VOCs diffused in nitrogen. Such a mixture is not explosive at any VOC concentration because of the absence of a significant concentration of oxygen. No vapor stream conditioning would be necessary if such a tank car were subsequently loaded under sealed hatch conditions.

Railroad tank cars are cleaned between unloading and loading if the tank has been contaminated in some way, or if the VOL to be loaded differs chemically from the VOL previously loaded. Tank cars which have been cleaned will have little or no VOC in the tank. Sealed hatch loading of a clean car would not require conditioning of expelled vapor if the tank car interior was purged with nitrogen as a final step in the cleaning process, or purged with nitrogen prior to loading, as is frequently done.

There are some cases however, where vapor conditioning of the vapors collected from loading of VOL into railcars would be appropriate to ensure safe operation.

Saturation of Vapor Stream with VOL. The equipment used for vapor stream saturation is, in its simplest form, a chamber incorporating nozzles through which VOL may be injected as a mist into the VOC stream to be saturated. To achieve maximum efficiency, VOL is usually injected countercurrent to the flow of the VOC stream, and baffles are frequently included in the saturator to increase turbulence and promote maximum vapor-liquid contact. The saturator should be located as near as possible to the VOC collection point to minimize the distance over which a potentially explosive VOC stream is transported before saturation.

The VOL saturant may differ chemically from the VOC in the vapor stream to be saturated. The VOL saturant is selected on the basis of cost, volatility, availability, and compatibility with the vapor stream to be saturated.

Dilution of Vapor Stream with Air. In diluting the VOC stream collected from the railcar during the loading operation, the VOC stream is discharged into ductwork leading away from the collection point(s) (Figure 12-7). Air is drawn into the ductwork upstream from the collection point(s) by a blower located downstream from the collection points. The ductwork and blower are sized to dilute the maximum possible amounts of collected VOCs to 25 percent LEL.

This ductwork collection system provides immediate dilution of the VOC stream at its point of collection, and safe transport of the VOC stream away from the terminal. Considering that VOC vapor streams from loading of railroad tank cars are frequently of VOC concentrations near or above the UEL, considerable dilution with air is required to reduce these concentrations to 25 percent LEL. Consequently, large volumes of dilute VOCs are produced, and cost of control or destruction is increased significantly.

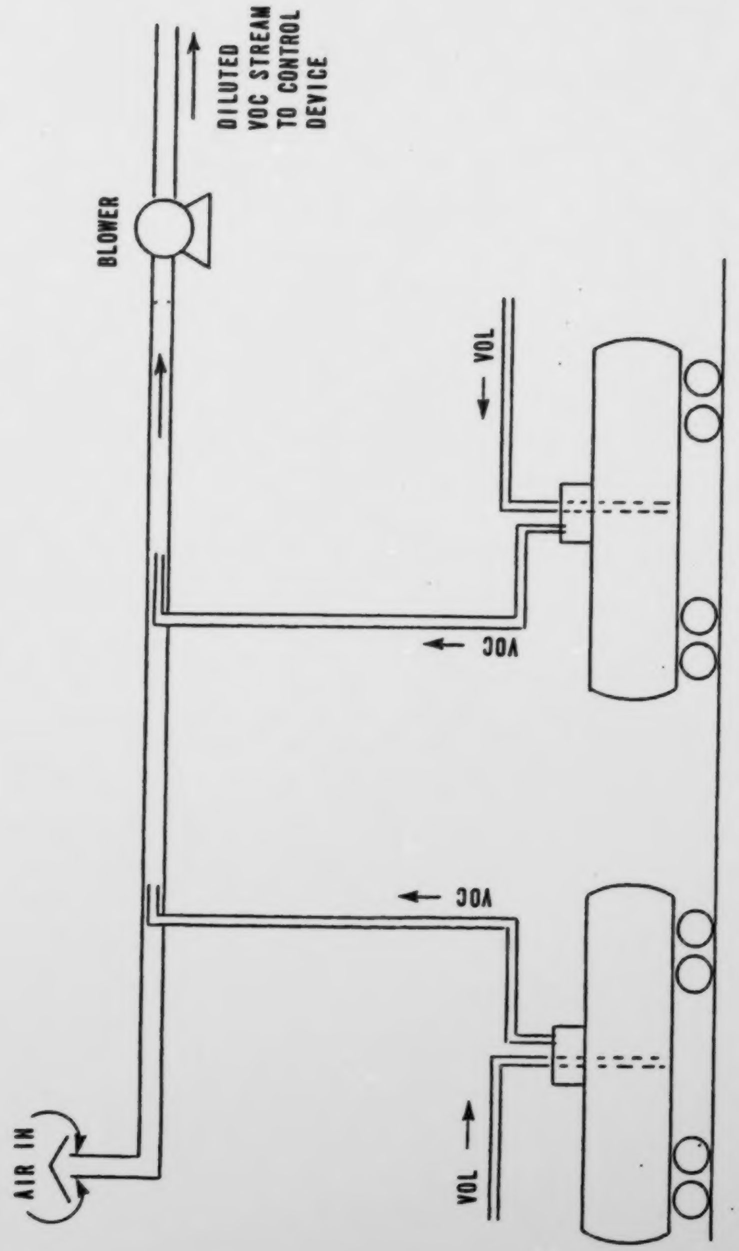
Vapor Control And Destruction Equipment

Although a number of emission control techniques can be used to reduce VOC emissions from tank car loading, incineration and flaring are the most common.

Prior to flaring, however, the VOC's which have been saturated (or which were above the UEL concentration as collected) are frequently stored temporarily in bladder storage tanks, or are vented to the vapor space of the intermediate VOL storage tank from which the loaded VOL was drawn. Because of the large volumes involved, VOC streams which are diluted during the collection process are not held in temporary storage before destruction or control.

FIGURE 12-7

DILUTION OF COLLECTED VOC WITH AIR DURING VOL LOADING OF RAILROAD TANK CARS


BLOWER
DILUTED VOC STREAM TO CONTROL DEVICE
VOL
VOC
VOC
VOL
AIR IN

The purpose of the bladder storage tank is to accumulate and store the irregular flow of VOC emissions from the intermittent tank car loading operations, thus evening out the surges and lulls in the flow of VOC's to the control device. The storage tank consists of a tank which contains an expandable bladder. Following saturation, the VOC's flow to the storage tank under pressure, inflating the expandable bladder. When the bladder has expanded to pre-set volume, the VOC stream flows to the control device.

VOC's vented to the vapor space (vapor balanced) of the intermediate storage tank from which the loaded VOL is drawn are considered to be in temporary storage. These vapors are emitted when the storage tank is refilled with VOL. Since this emission point is remote from the railcar loading terminal, however, control or destruction of these emissions is not considered here.

Thermal incineration and flaring are the usual methods for controlling VOC emissions from loading of VOL's into railroad tank cars.

Catalytic oxidizers are not as widely used as thermal incinerators because the catalysts can be poisoned by sulfur-and halogen-containing compounds.

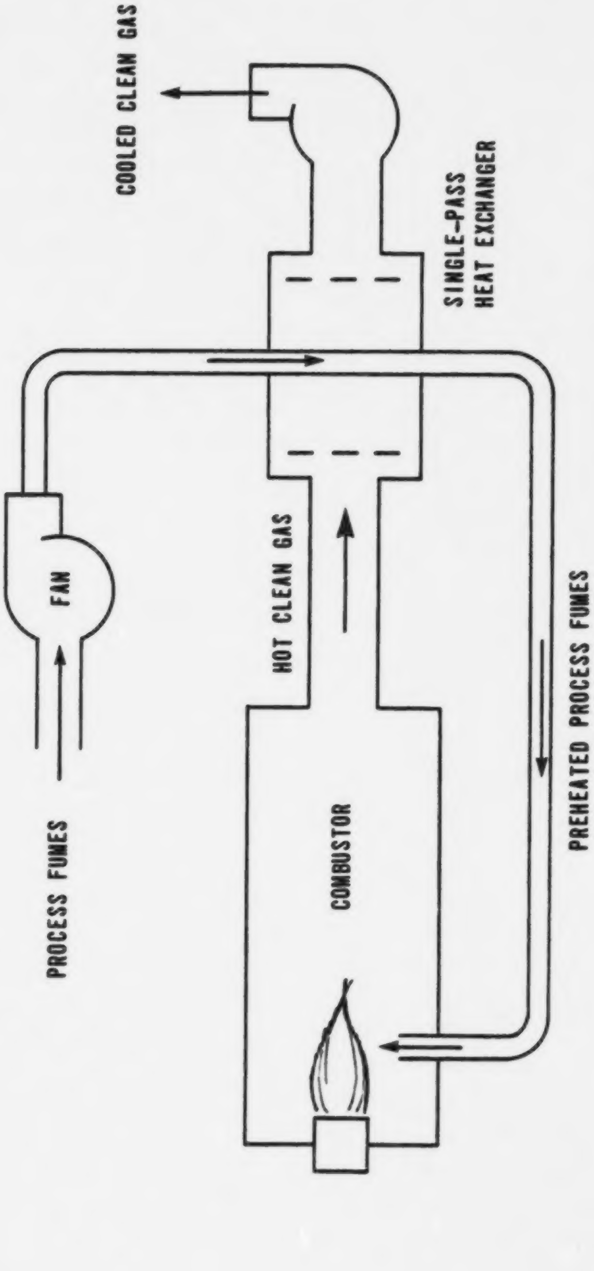
Thermal incineration is a widely used method for control of VOC emissions from railroad tank car loading of VOL's because it is applicable to a variety of chemicals and VOC vapor stream conditions. Incineration is commonly the method of control for streams with heating values below the LEL.

A thermal incinerator is usually a refractory-lined chamber containing a burner at one end and generally operated at about 760°C (1400°F) with a residence time of from 0.3 to 1 second8) (Figure 12-8).

Combustion chamber temperature is an important parameter in the design of a thermal incinerator, since oxidation rates are highly temperature-dependent. Incineration of a low heating value VOC vapor stream necessitates the burning of an auxiliary fuel to achieve the desired chamber temperature. Destruction of VOC's with about 90 percent efficiency occurs rapidly at temperatures over 760°C (1400°F).

FIGURE 12-8

THERMAL INCINERATOR


COOLED CLEAN GAS
SINGLE-PASS HEAT EXCHANGER
FAN
HOT CLEAN GAS
PROCESS FUMES
COMBUSTOR
PREHEATED PROCESS FUMES

Mixing is crucial in achieving good thermal incinerator performance. A properly designed incinerator will rapidly combine the VOC, combustion air, and hot combustion products from the burner to ensure that the VOC will be in contact with sufficient oxygen at a temperature high enough to start the oxidation reaction. Improper mixing can enable pockets of VOC to pass through the incinerator intact and can lead to poor temperature distributions where not all the VOC vapor stream reaches or remains at the combustion temperature.

Residence time is the time available for the oxidation reaction to occur within the combustion chamber. Residence times from as low as 0.3 seconds to several seconds have been used in thermal incinerator design[9)].

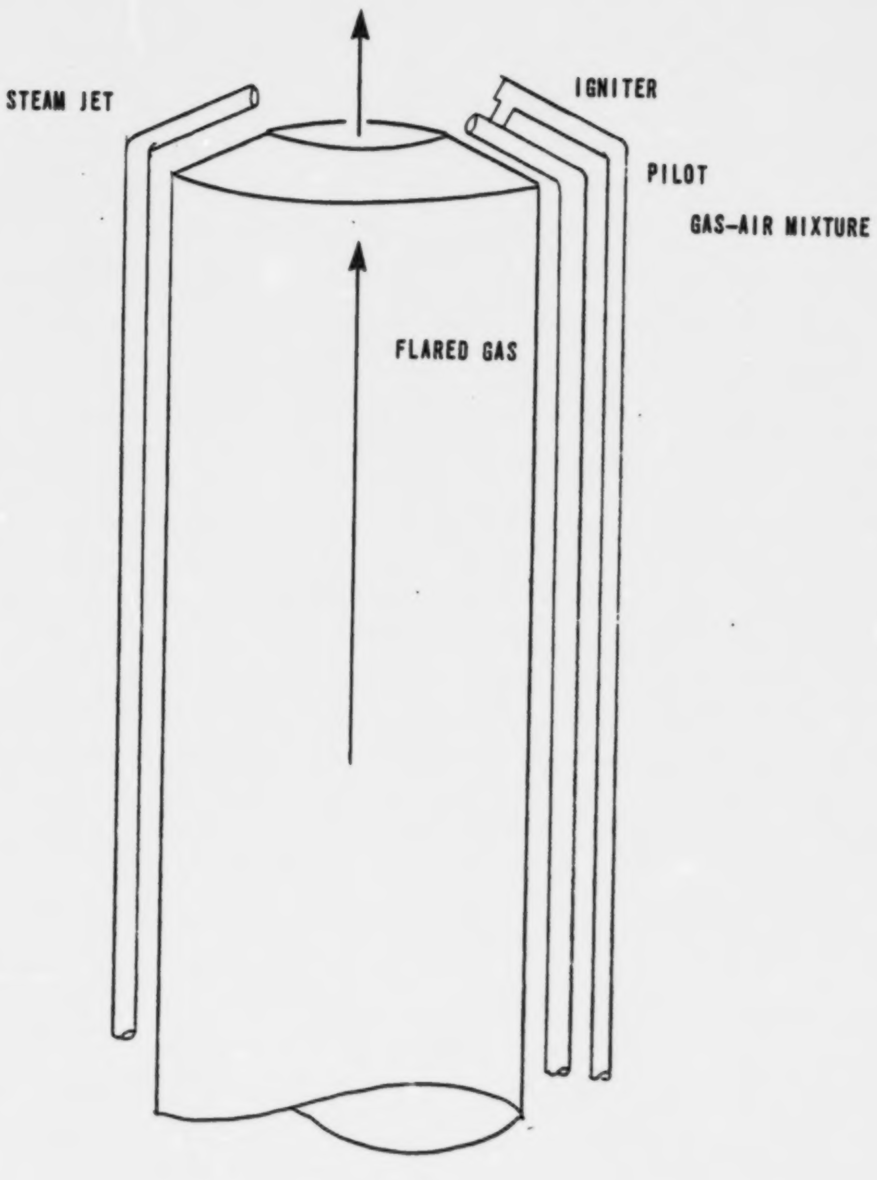
Based on a study of thermal oxidizer efficiency, cost, and fuel use, 98 percent VOC reduction is the highest reasonable control level consistently achievable by new incinerators, considering current technology[10)]. This degree of VOC reduction is based on thermal incinerator operation at 870°C (1600°F) and 0.75 second residence time.

Flaring is generally used in the petroleum and chemical industry as a means of controlling rapid and unexpected releases of combustible gases. Flares can handle a wide variation in gas flow rates and gas heat capacities. The concentration of VOC's in vapors to be flared is frequently greater than the upper explosive limit.

Flares are generally less expensive to install and operate than thermal incinerators. Flares are also generally noisier than incinerators and can produce vibrations which may be considered a nuisance.

There are three types of flares; elevated, ground, and pit. Elevated flares are most common (Figure 12-9). As in all combustion processes, time, turbulence, and temperature control the effectiveness of combustion. Flared gases must be kept at or above their auto-ignition temperature to combust completely. The turbulence is sometimes supplied by steam injection at the ports in the stack. Time is controlled by the rate of release of the flared vapor.

ELEVATED FLARE


STEAM JET
IGNITER
PILOT
GAS-AIR MIXTURE
FLARED GAS

Flared VOC vapor streams are ignited by a pilot light just as they reach the top of the stack. Before thorough mixing can occur, part of the VOC vapor may burn. This may cause an oxygen deficiency which can result in carbon formation. The as-yet-unburned VOC vapors may also "crack" to form smaller reactive molecules of olefins and paraffins, which may allow some molecules to polymerize into long chain hydrocarbons. More carbon may be created from the combustion of these long chain hydrocarbons. Steam injection can reduce the amount of carbon formation by the mixing action resulting from its injection. Reduction in the amount of carbon produced will help to eliminate flare smoking problems. For VOC vapor streams with heating values below 100 Btu/ft$^{3,11)}$ auxiliary fuel may be required for effective combustion.

The design of a flare depends on the VOC vapor stream to be flared. The actual VOC composition of the vapor stream effects the time, turbulence, and temperature requirements for complete combustion. The temperatures of combustion can be controlled by adding supplemental fuel and additional pilot lights. The turbulence can be controlled by flare stack design and steam injection. The time of burning can be controlled by flare stack design and VOC vapor stream flow rates. Flow rates to the flare are controlled through design and pre-set operation of the temporary storage bladder tank which provides even flow rate of the VOC vapor stream to the flare.

To ensure ignition and provide good flame stability the normal operating range of a flare should be 1-5% of its maximum capacity. The pilot light must be able to withstand high wind and heavy rain. The steam injection requirements to prevent smoking depends upon the hydrogen to carbon ratio of the VOC. A hydrogen to carbon ratio of 0.33 requires no steam injection, but a hydrogen to carbon ratio of 0.25 may produce smoke and therefore requires steam injection. The height of the flare is dictated by heat, fire, and safety considerations.

The available information on flare efficiency is very limited because of the difficulty of measuring VOC emissions from flares. Literature data indicates that flare efficiency may vary from as low as 60% VOC destruction to as high as 99.9% VOC destruction.

Costs

To develop information on approximate cost of VOC emission control by incineration for railroad tank car loading terminals, cost effectiveness calculations have been performed on acetone, a typical VOL frequently loaded into railroad tank cars. The vapor pressure of acetone approaches the weighted average vapor pressure of the diverse VOL's included in the responses to a a partial industry survey4) covering the railroad tank car loading industry. Calculations were based on annual loading volumes spanning the range of throughputs found in typical railroad tank car loading terminals. In this example the acetone emissions were collected by dilution. The results of these calculations are tabulated in Table 12-3, and the cost effectiveness results are presented graphically in Figure 12-10, which shows that cost of control decreases as volume of VOL loaded in the terminal increases. The cost effectiveness modeled in this example reflects the control of characteristic amounts of VOC's emitted in typical railroad tank car loading operations, and should not be construed as typical cost effectiveness values for incineration in other applications.

STATUS OF REGULATORY ACTIVITIES

Regulations covering control of emissions from tank car loading of VOL's for those States which presently do not meet the national ambient air quality standards for ozone, and which have been granted extentions beyond Dec 1982, have been reviewed. Several of those states currently require the recovery or destruction of vapors emitted as a result of railcar loading of VOL's. Six States, however do not require this operation to be controlled, while nine others limit the scope of the requirement to the loading of gasoline. Still others require only that loading be accomplished by means of bottom filling or by submerged fill pipe. Those that require the recovery or destruction of VOC's have basically used as a guide the control techniques guideline for the loading of gasoline into tank trucks.

TABLE 12-3

EXAMPLES OF COSTS AND COST EFFECTIVENESS FOR THERMAL INCINERATION OF VOC'S FROM RAILROAD TANKCAR LOADING

Example	I	II	III
VOL loaded	Acetone	Acetone	Acetone
MM gallons loaded/year	4	18	42
Equipment cost	$ 60,000	$68,000	$80,000
Installation costs	37,000	41,000	49,000
Piping and ducting	4,000	8,000	19,000
Taxes, freight, and instrumentation	11,000	12,000	14,000
Total installed capital cost	$112,000	$129,000	$162,000
Direct			
Operating labor	$1,500	$1,500	$ 1,500
Maintenance labor	2,000	2,000	2,000
Electricity	100	200	500
Natural gas	2,000	4,000	11,000
Subtotal	$5,400	$7,400	$15,000
Indirect			
Capital recovery[a]	$16,000	$21,000	$26,000
Taxes, insurance & administration[b]	4,000	5,000	6,500
Subtotal	$20,000	$26,000	$32,500
Total annualized cost[c]	$25,400	$33,400	$47,500
Tons controlled VOC emissions/year	4.5	20	47
Cost effectiveness	$5600/ton	1700/ton	$1000/ton

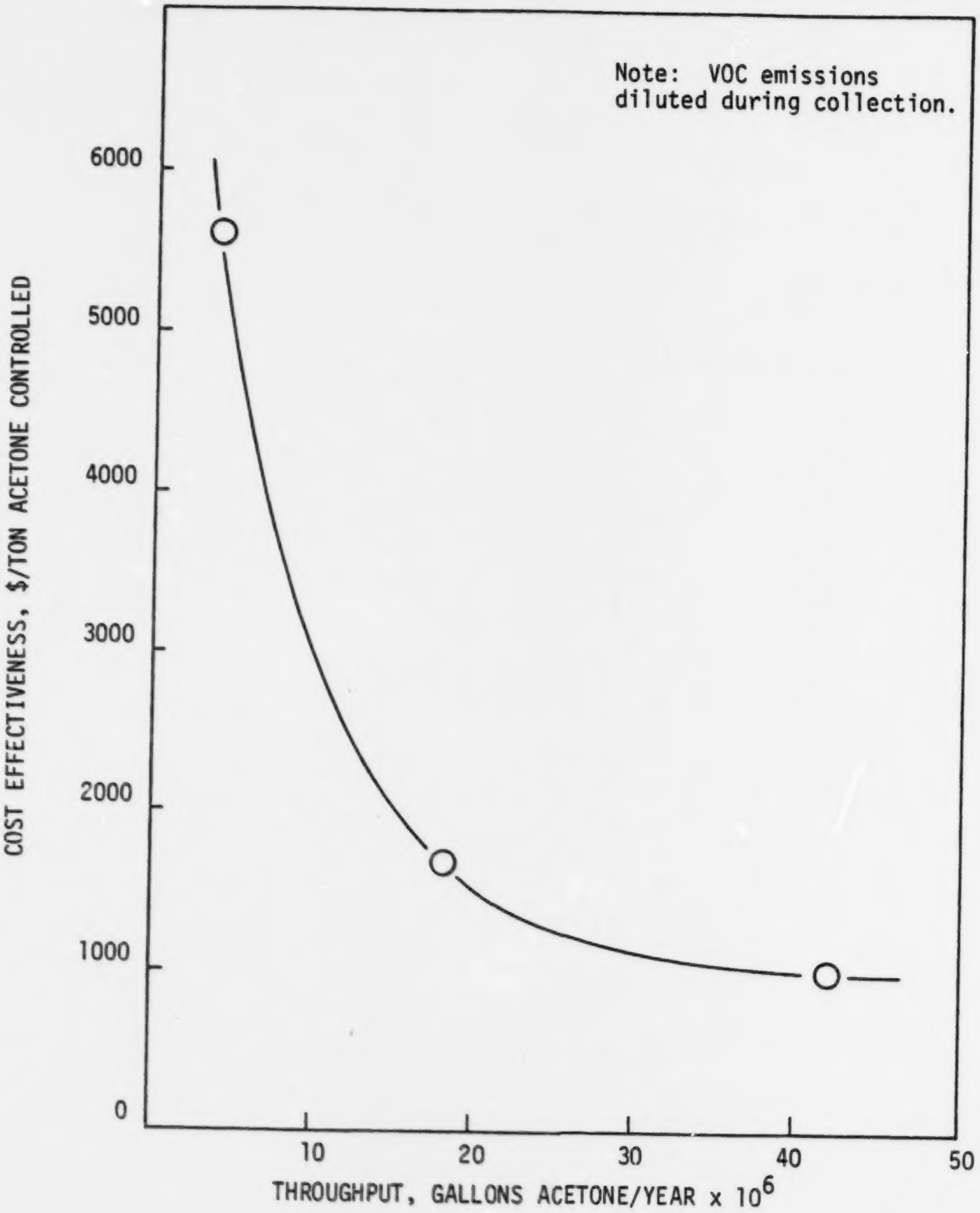
[a] Capital recovery factor of 16.275 percent of total installed capital cost. Based on 10 year life of incinerator and 10 percent interest rate.

[b] Four percent of total installed capital cost.

[c] Direct subtotal + indirect subtotal.

Note: All costs are rounded to the nearest $100, and are in 1980 dollars. No heat recovery from the incinerator is included in these example calculations.

COST EFFECTIVENESS FOR CONTROL OF ACETONE EMISSIONS DURING RAILROAD TANK CAR LOADING



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SECTION 13

SOLVENT EXTRACTION PROCESSES

PROCESSES AND EMISSIONS

The extraction of fats and oils is accomplished through rendering, pressing and solvent extraction. The process to be used is determined by the characteristics of each oil-bearing material. Tallow and grease from fatty animal tissues is recovered by rendering as are marine oils from fish and whale blubber. Mechanical expression (by continuous pressing or centrifugal expression) is used to obtain the major portion of the oil from various oil seeds such as copra, sunflower seeds, castor bean, and peanuts, as well as from fruit pulp, generally olives. This process is also used to recover oil from rendering residues. However, for maximum recovery of oil from oil seeds, extraction is done especially with oil seeds having a low oil content. The final recovery of the oil is accomplished through mechanical expression. Soybeans are almost always exclusively solvent extracted directly. A process called "prepress solvent extraction" is used for cottonseed, flaxseed, and for high oil content seeds, including copra, peanuts, corn germ, castor beans, sunflower seeds, olives and wheat germ.

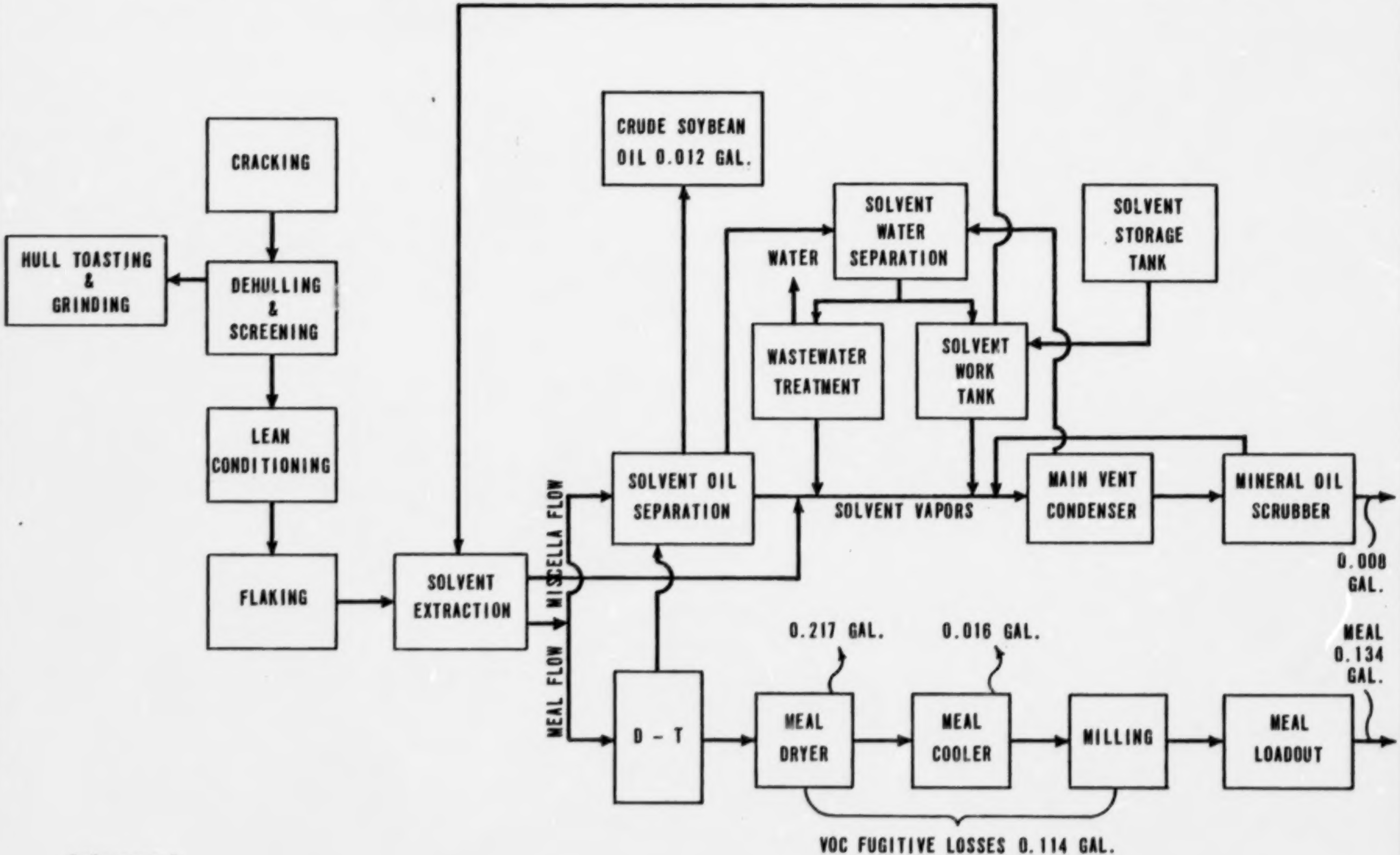
Soybean Oil Extraction

The emphasis in this section will be on soybean oil extraction since, according to the Research Triangle Institute (RTI), 80 percent of all the vegetable oil produced in the United States is extracted from soybeans1). Finelt of Fluor Engineers and Constructors reports that soybean oil accounts for 60 percent of the total food use of fats and oils2).

Soybean oil is obtained through solvent extraction via hexane. This is a continuous processing operation (see Figure 13-1). This figure illustrates a typical plant operated to produce crude soybean vegetable oil and a soybean residue meal suitable for ultimate use as animal feed. Mechanical pretreatment of soybeans containing about 18 percent oil is required to facilitate the separation of the oils from the solids. In mechanical pretreatment, foreign materials are removed, the beans are

FIGURE 13-1

SCHEMATIC OF A SOYBEAN PROCESSING PLANT – VOC EMISSION SOURCES (gal/ton of raw soybeans processed)



CRACKING
HULL TOASTING & GRINDING
DEHULLING & SCREENING
LEAN CONDITIONING
FLAKING
SOLVENT EXTRACTION
MISCELLA FLOW
MEAL FLOW
CRUDE SOYBEAN OIL 0.012 GAL.
SOLVENT OIL SEPARATION
WATER
SOLVENT WATER SEPARATION
WASTEWATER TREATMENT
SOLVENT WORK TANK
SOLVENT STORAGE TANK
SOLVENT VAPORS
MAIN VENT CONDENSER
MINERAL OIL SCRUBBER
0.008 GAL.
D – T
0.217 GAL.
0.016 GAL.
MEAL DRYER
MEAL COOLER
MILLING
MEAL LOADOUT
MEAL 0.134 GAL.
VOC FUGITIVE LOSSES 0.114 GAL.

Reference 3

dehulled, reduced in size and crushed. Prepared soybeans are then fed directly to an extractor where they are then introduced to a series of washings with warm hexane solvent to extract the vegetable oil. The solvent must then be removed from the oil in the solvent recovery section by means of multiple stages of evaporation and stripping. The crude soybean oil is stored and the recovered hexane solvent is passed to a solvent work tank. The recovered hexane is recycled and used again at the extractor.

As the meal (soybean residue) leaves the extractor, it is subjected to a stream stripping operation in the meal desolventizer. This removes most of the hexane retained in the meal. The water-hexane vapors, in addition to the liquid solvent and oil, are passed to the solvent recovery section for oil separation and solvent recovery, while desolventized meal is dried and cooled to produce a soybean meal product.

Process Emissions and Emission Points

There are three vent streams containing hexane which are discharged to the atmosphere during soybean processing. These three emission points are: (1) the main vent stream issuing from the solvent recovery section, (2) the dryer vent stream issuing from the meal dryer, and (3) the cooler vent stream exiting from the meal cooler (see Figure 13-1).

The incentive to reduce hexane emissions to the atmosphere at soybean processing operations is high since hexane is expensive, thus making recovery operations very desirable. The profit is dependent to a large extent upon keeping the hexane losses as close to zero as possible in extraction operations. In most cases, according to RTI, 99.9 percent of the hexane is recoverable. The remaining 0.1 percent which is lost to the atmosphere, at first glance may not seem like a significant amount to the industry; however, in terms of total hexane emissions as an air contaminant, this 0.1 percent can be highly significant. This is so because the typical operational ratio of hexane weight to dehulled oil seed weight is about one to one. Obviously, the larger the operation, the greater the hexane emissions.

CONTROL TECHNOLOGY

As reported by Finelt in the November 1979 APCA Journal, the losses of total hexane to be expected from soybean processing plants may vary from 0.5 gals./ton of soybean processed up to 5.0 gals./ton, with a mid-range of 0.7 to 2.7 and an average of about 1.0 to 1.4 gals./ton. As would be expected, the newer plants tend to have lower emissions due to the incorporation of additional hexane collection equipment such as a mineral oil adsorber/stripper unit to the main vent stream. Assuming an average value of 1.2 gals./ton and 18 percent oil in soybeans, Table 13-1 shows that in 1977, approximately 29.5 MM gals. of hexane were discharged to the atmosphere as a result of soybean process operations2).

As mentioned previously, the consideration of emission points at such an operation can be summed up as follows: the main vent stream and a combined dryer/cooler vent stream. These later two can be combined due to the similarities of their origins and the low potential hexane content of each stream. Table 13-2 presents the expected flow quantities of the two vent streams from any given soybean plant. It is anticipated the air pollution abatement facilities that would be installed would reduce the hexane level of the emitted stream to 100 ppm or less2).

The two primary air pollution abatement systems which could be applied to soybean processing operations are thermal oxidation and mineral oil adsorption (currently the most widely used).

Thermal oxidation systems possibly applicable for the reduction of hexane emissions from solvent extraction include direct thermal incineration and catalytic oxidation. However, vent streams from the dryer and cooler contain particulate matter which could foul the catalyst in a catalytic oxidation system2). Thus, direct thermal incineration appears to be the most feasible of two oxidation approaches. Because uncontrolled VOC emissions from the dryer and cooler are rather low in concentration, the cost-effectiveness of thermal oxidation would be rather poor unless emissions from the dryer/cooler vents were combined with those from the main vent condenser. One other alternative oxidation approach would be to vent VOC emissions from the dryer/cooler vents to the plant's main boiler.

TABLE 13-1

PRODUCTION OF SOYBEAN OIL IN U.S.

Year	MM lb.	Year	MM lb.
1960	4392	1971	8082
1965	5236	1972	8084
1966	5811	1973	7540
1967	6150	1974	8705
1968	6150	1975	7862
1969	6805	1976	9640
1970	8086	1977	8836

TABLE 13-2

COMPOSITION OF VENT STREAMS FROM SOYBEAN PROCESSING PLANTS

	Main Vent	Combined Dryer/Cooler Vents
Solvent	Hexane	Hexane
Air Volume, ACFM	1070	55860
Temperature (°F)	80°	210°
Quantity of Solvent, lb./day	209-20900	397-39750

Reference 2

Carbon adsorption has been considered as a VOC control technique and a few systems have been installed on solvent extraction plant vent streams. However, high cost and the potential risk of fire and explosion have made these systems unattractive to industry.

According to a draft Background Information Document (BID) prepared on Vegetable Oil Processing for the U.S. Environmental Protection Agency, the most widely used VOC control system on solvent extraction main vents is the Mineral Oil Scrubber3). These scrubbers can control main condenser vent VOC emissions at an efficiency of about 95 percent.

The type of oil used for hexane absorption is white mineral oil of technical grade with a molecular weight of between 290 and 330, and a viscosity at 100°F of 50/60 second Saybolt Universal. This recovery process is located at the main vent and is reported to be approximately 95 percent efficient1).

Volatile organic compound losses occur throughout the process in varying amounts. In addition to the emissions of the main vent, the dryer vent also can experience considerable VOC losses. It is possible that the hexane concentration at the dryer vent can be in the flammable range. At present there is no applicable recovery technology for this particular vent, according to Chessin of RTI1).

Fugitive loss of VOCs (which are not proportional to plant size3)) vary greatly from operation to operation. Generally, they range from 0.13 gals./ton of soybeans processed to 0.33 gals./ton.

Fugitive emissions result from motor driven shafts with packing glands and stuffing boxes of solids processing units, sight glasses, cleanouts, and access doors also leak vapor if they are not maintained.

Control Technology Costs

Solvents such as the commonly used hexane are expensive, and efficient solvent recovery is favorable for both air pollution abatement and for the reuse of the solvent.

Using the soybean industry as an example of a solvent recovery operation, volatile organic compound losses to the atmosphere can amount to about 0.5 percent of the original quantity used3). In 1979, the mid price for the solvent was $0.70/gal.2). In a reasonably well-operated plant, operating at 1,000 tons/day production, the solvent losses can amount to 3.15 gals./ton of soybeans processed3). This amounts to a dollar loss of $2,205/day (this is in about the mid-range for VOC losses, as discussed earlier in this section)

Available control cost data were investigated for three control alternatives; these were: an activated carbon adsorber on the main vent or combined with the dryer/cooler vent and treated as a whole; a thermal incineration unit on the combined dryer/cooler vent, or combined with the main vent and incinerated together2); finally, the mineral oil scrubber, which is considered by the EPA to be an integral part of the entire process and not necessarily an add-on abatement technique.

The cost (in 1979) for a carbon adsorption system is approximately $108,200, with operating costs of $67,860 to $102,420 per year, depending on the amount of hexane to be handled (209 lbs./day or 1,045 lbs./day, respectively2)). With this type of abatement equipment, the losses of hexane can be reduced to less than 0.5 gals. per ton of soybeans process2).

According to a representative of the Petroleum Branch of the Environmental Protection Agency, the cost of a thermal incineration unit on the main vent is $69,500 and $101,200 on the dryer vent. However, hexane revenues are not realized until the hexane content exceeds 18,000 lbs./day.

As for the cost of a mineral oil scrubber, this particular type of equipment is so integrated into the total operation, it would be difficult to single out the price of the unit, its installation or its operational costs, as reported by a representative of the Petroleum Branch of the EPA where considerable cost analysis has been done on such equipment.

Coffee Roasting and Decaffeination

Thirty percent of the coffee beans processed in the United States are used for instant coffee and only five percent of the beans are used for decaffeinated coffee. The majority of the beans are simply cleaned, blended, roasted, and packaged for sale$^{4)}$.

Volatile organic compounds are emitted during the roasting and decaffeination processes. A direct-fired afterburner operating in a range of 650 to 750°C (1200-1400°F) will almost completely eliminate the emissions from the continuous batch roasters. Prior to roasting, decaffeination is accomplished with trichloroethylene. As of 1974, 1,500 tons per year of volatile organics were emitted to the atmosphere. For the solvent loss (trichloroethylene) which is the major emission, there is no control technique used$^{4)}$.

STATUS OF REGULATORY ACTIVITIES

Currently, the Fresno County Air Pollution Control District (California) has a rule (No. 409) on organic solvents. However, if the solvent does not come in contact with a flame, the particular process is exempt from the rule. The South Coast Air Quality Management District (SCAQMD [California]) also has a rule on organic solvents and the associated emissions (No. 442).

Similar to the Fresno County rule, the SCAQMD exempts those industries utilizing organic solvents under certain conditions such as having the emissions reduced by 85 percent or the following:

(1) Organic materials that come into contact with flame or are baked, heat cured or heat polymerized, are limited to 1.4 kilograms (3.1 pounds) per hour not to exceed 6.5 kilograms (14.3 pounds) per day.

(2) Organic materials emitted into the atmosphere from the use of photochemically reactive solvents are limited to 3.6 kilograms (7.9 pounds) per hour, not to exceed 18 kilograms (39.6 pounds) per day, except as provided in subsection (a)(1).

All organic materials emitted for a drying period of 12 hours following their application shall be included in this limit.

(3) Through and including November 30, 1980, organic materials emitted into the atmosphere from the use of non-photochemically reactive solvents are limited to 180 kilograms (396 pounds) per hour not to exceed 1350 kilograms (2970 pounds) per day, except as provided in subsection (a)(1). All organic materials emitted for a drying period of 12 hours following their application shall be included in this limit.

(4) On and after December 1, 1980, organic materials emitted into the atmosphere from the use of non-photochemically reactive solvents are limited to 36.8 kilograms (81 pounds) per hour not to exceed 272 kilograms (600 pounds) per day, effective December 1, 1980.

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SECTION 14

SURFACE COATING OF LARGE AIRCRAFT

PROCESSES AND EMISSIONS

Aircraft coating operations are centered about major aircraft manufacturing and repair centers in the United States. In the South Coast Air Quality Management District (SCAQMD [Southern California]) the coating of aerospace components (a term used by the SCAQMD including aircraft coating) alone contributes 4.4 tons per day of volatile organic emissions.

Painting operations result in the generation of several types of contaminants: various quantities of nonvolatiles (solid or semisolid nonorganic materials) and vapors of organic solvents. These volatile organic compounds (VOCs) are not captured and retained by air filters or waterfall curtains typically used for particulate control[1,2,3]. In the case of aircraft painting and coating, afterburners or incinerators essentially do not play a role in pollution abatement efforts[4,5]. However, activated carbon adsorption has recently been applied as a method of VOC abatement in aircraft coating.

The aviation industry, from an operational point of view, is generally classified into three categories: commercial, general service, and military. For the most part, commercial aircraft are large multi-engine fixed-wing airplanes. Planes used in general service are generally much smaller, with many in the single engine, two or four passenger category. There are also increasing numbers of 6 to 20 passenger aircraft used for business purposes. Military aircraft cover all sizes and types, from light single engine planes to the largest multi-engine cargo planes. A variety of helicopters are also in the military category. Coatings used for military aircraft must meet military specifications. Most military aircraft are coated with flat camouflage paints as compared to the gloss decorative paint used on civilian aircraft.

From a point of view of coatings and coating application methods, the most important distinguishing features seem to be (1) size of aircraft, and (2) whether the aircraft is for civilian or military use. Painting operations of both small and large aircraft manufacturers are described here.

Three manufacturers of light aircraft (Beechcraft, Cessna, and Gruman) reported that very few, if any, of the exterior components of the aircraft come to them prepainted or even preprimed. Prior to assembly, light aircraft components are generally coated with two primers and a topcoat. The first coat is called a filling primer which smooths out the surface of the component; the second coat is an anticorrosion primer which is applied to protect the surface of each exterior component; finally, the topcoat (either clear or colored) is applied for the final protection and decoration of the craft. Most light aircraft, however, have colored (pigmented) topcoats.

Both the primers and the topcoat use MEK, MIBK, or toluene as solvents. The primers are of the epoxy-polyamide type and the topcoat paint is generally a polyurethane.

Depending on the normal practice of the aircraft manufacturer, the first primer coat is applied either electrostatically in an automated fashion within a waterfall booth, or is conventionally sprayed with compressed air. The second primer and the topcoat are both applied using a hand-held compressed air spray gun. This process is also done in a waterfall booth. The air from the painting area is filtered, and the water from the waterfall booth is subjected to paint reclaiming (paint is disposed of) and then is recycled. These two control methods are well suited to the capture of particulates, however, the volatile organic compounds are not captured by these methods.

Large aircraft are generally painted with only one primer coat and one topcoat. Both of these coatings are applied by the conventional compressed air spray in a controlled environment paint hangar. In essence, this means that hangar inlet air is filtered.

Large aircraft are usually painted as an entire unit. there is one epoxy-type primer coat and one polyurethane topcoat. Some airlines prefer their planes without color, and as such are coated with a protective acrylic prior to the riveting; this coating is then removed after the assembly of the craft. The sheet stock is polished aluminum coated with "Alodine™" which allows the metallic finish of the craft to show through.

The solvents used are generally MEK and toluene, however, there are many blends which may contain any combination of ketones, alcohols, and glycol ethers6).

In the case of at least one manufacturer (Lockheed) the wings are painted prior to attachment to the fuselage. In addition, they use two primer coats, one called a wash primer which is approximately 85 percent solvent. This does present a high potential for volatile organic losses; however, according to a finishes expert at Lockheed, the amount applied per unit area is low. The second primer is an intermediate coat, a polyurethane which is high in solids, as is the following topcoat which is a polyesterurethane. The process used for applying the primers and the topcoat involves a gantry on wheels which runs along a track. Several painters positioned on each side of the gantry at different levels use compressed air spray guns for even paint application. The wings are painted in the open area of the hangar. Fans are used to direct the over-spray toward the fiberglass filters. According to a contact at Lockheed in Burbank, California, it is a general practice for most airlines to completely strip off the old primer and paint and reprime and repaint the aircraft every five years.

As with all surface coating operations, the emissions of volatile organic compounds are dependent upon VOC content of the coating, the amount of coating applied, and the efficiency of the application method in transferring the coating to the object to be coated. No detailed emission factors are available for this category, but solvent-borne coatings similar to those used in coating other metal products are utilized. Coatings for main body and wing assemblies must be air dried. No waterborne coatings were found to be used at the present time.

CONTROL TECHNOLOGY

The surface coating of aircraft involves the coating of large irregularly shaped objects at relatively low production rates. This very nearly precludes the use of add-on controls for VOC losses because of the very large exhaust flow rates and flow VOC concentrations in the exhaust. Both capital and operating costs would be extremely high. Consequently, control techniques principally involve the use of high solids or waterborne coatings and the conversion to higher transfer efficiency coating application systems. There are some special problems relating to aircraft coatings which have an impact on the ability to change coating formulations. These include the importance of corrosion resistance, the need to tolerate high altitude exposure conditions (extreme temperature ranges and high levels of ultraviolet radiation), and the need to meet military specifications on a portion of the aircraft manufactured.

Tinker Air Force Base (Oklahoma City, Oklahoma) has the most modern aircraft painting hangar presently in operation. The hangar, which can accomodate the painting of two aircraft the size of a 747 simultaneously, was designed with two carbon adsorption air pollution abatement units at either end of the building.

This hangar, which went operational in 1979, was designed with the control equipment to facilitate compliance with volatile organic compound regulations. Each carbon adsorber contains three large activated carbon canisters each, with eighteen smaller canisters. The two units combined move 136,000 CFM of air through their filters. Approximately 90 percent of the air in the hangar is recirculated, requiring only about 10 percent make-up air.

According to representatives of Tinker Air Force Base7), the carbon adsorption units are effective, but would be even more efficient if the steam used to regenerate the carbon was at a higher temperature than the 250°F steam now used. Presumably this would aid in stripping higher boiling point solvents. No test data were reported.

With these two particular units, the carbon is regenerated every 8 or 9 hours; however, it could maintain its efficiency for as long as 16 hours without regeneration.

The only major problem encountered so far has been with the small canisters becoming clogged with paint from overspray. In response to this, Tinker Air Force Base plans to install bag filters to catch the overspray that the water-wash booths do not capture.

Coating specification data obtained during this study shows volatile organic compound content in coatings ranging from about 30 to 90 percent by volume range. Reductions in VOC content of aerospace coatings used in the Los Angeles Basin area (South Coast Air Quality Management District) are scheduled to begin in August 1982 with a further reduction of VOC content in primers in 1985 (see Rule 1124 in Status of Regulatory Activities below). The estimated reduction will be partially accomplished by using high solids coating in 1982 and waterborne coating for primer in 1985. The estimated cost of the 1124 SCAQMD rule is approximately $16,000 per ton of organic emissions reduced.

The application of coatings with improved transfer efficiency could be considered equivalent to VOC control using high solids or waterborne coatings. Application methods utilizing electrostatic coating, hydraulic spray equipment, and special low air volume spray guns (sometimes described as mistless sprayers) are possible alternative approaches. Reduction in paint use of 50 percent or more are thought to be achievable with some of these methods.

It was suggested by the Board of the SCAQMD that aircraft coating could be eliminated altogether, thereby dramatically reducing organic emissions. However, representatives of the aircraft manufacturing industry expressed the concern that hand-polishing the bare metal surface (in order to keep it smooth for flight) was too costly due to the required number of person-hours and the price of labor.

STATUS OF REGULATORY ACTIVITIES

Several states maintain regulations on volatile organic compound emissions from the coating industry, however, these rulings do not apply specifically to aircraft coating.

The SCAQMD (Los Angeles Air Basin) in July 1979 proposed its Rule 1124, Aerospace Assembly and Component Coatings Operations. Its requirements are stated as follows:

"(b) Requirements

(1) After August 1, 1982, a person shall not:

(A) Apply to aerospace components any primer or topcoat which contains volatile organic compounds in excess of:

(i) 650 grams per liter of primer less water, as applied.

(ii) 600 grams per liter of topcoat less water as applied.

(B) Apply to aerospace components any temporary protective coating that contains more than 250 grams of volatile organic compound per liter of material less water, as applied.

(C) Use volatile organic compounds of composite vapor pressure of 77.6 mm Hg (1.5 psia) or greater at a temperature of 21.1°C (70°F) for surface preparation or cleanup, excluding paint removal.

(D) Use other than closed containers for disposal of cloth or paper impregnated with solvent containing volatile organic compounds which are used for surface preparation cleanup and paint removal.

(E) Use volatile organic compounds for the cleanup of spray equipment used in aerospace component coating operations unless 85 percent of the volatile organic compounds are collected and properly disposed such that they are not emitted to the atmosphere.

(F) Use stripper which contains more than 400 grams per liter of volatile organic compounds, or has a composite vapor pressure of volatile organic compounds more than 10 mm Hg (0.19 psia) at 21.1°C (70°F).

(2) After January 1, 1985, a person shall not apply to aerospace components any primer in excess of 350 grams per liter, less water, as applied.

(3) Until and including August 1, 1982, aerospace industry and aerospace components subject to the provisions of this rule shall comply with Rule 442 and any other applicable requirements of the Rules and Regulations of the South Coast Air Quality Management District.

(c) Equivalency

Notwithstanding the provisions of subparagraph (b) a person may comply with subparagraph (b) by reducing emissions from such coating operations provided that:

(1) The emission reducitons are at least equal to those which would be obtained by the use of coatings specified in subparagraph (b); and

(2) The emission reducition methods are applied to the coating operations subject to the provisions of this rule and are approved by the Executive Officer; and

(3) The owner or operator submits applications for new permits to construct or operate both basic and control equipment for such reductions.

(d) Methods of Analysis

The volatile organic content of coatings subject to the provisions of this rule shall be determined by the procedures detailed in Rule 107.

(e) Exemptions

(1) Until December 31, 1982, coating of aerospace assemblies and components procured by the Federal Government shall be exempted from the provisions of subparagraph (b)(1)(A) of this rule.

(2) The provisions of subparagraphs (b)(1)(A), and (b)(1)(B), and (b)(2) of this rule shall not apply to the following materials:

(A) Coatings for masking in chemical etching operations.

(B) Adhesive bonding paper.

(C) Flight test coatings.

(D) Space vehicles coatings.

(E) Fuel tank coatings.

(3) The provisions of subparagraph (b) of this rule shall not apply to the following materials:

(A) 1,1,1-Trichloroethane

(B) Methylene Chloride

(C) Trichlorotrifluoroethane

(4) The provisions of this rule shall not apply to a facility which emits a total of less than 9072 grams (20 pounds) of volatile compounds in any one day."

Additional existing air pollution control rules and regulations on the state and local level have not been specifically directed at this area of industry, but rather at VOC emissions in general.

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SECTION 15

SURFACE COATING OF LARGE SHIPS

PROCESSES AND EMISSIONS

There are about eight different types of marine coatings with application methods uniquely suited to each. These paint types include: epoxyamine, epoxypolyamide, polyurethane, vinyl, chlorinated rubber, alkyd, inorganic zinc, and acrylic. Table 15-1 presents each of these, and their applications and solids contents.

The aforementioned coatings are air dried and can be applied by brush, roller, or spray. The application of marine coatings and the associated solvents used for thinning and cleaning result in the emission of volatile organic compounds. On the California coast over ten tons per day of these compounds are emitted1).

Since marine coatings are applied to large surface areas and are dried in the open air, it is not practical to duct the emissions through abatement devices such as afterburners or carbon adsorbers.

Because of the stringent requirements of marine coatings, application characteristics vary with the type of coating. The properties which must be evaluated are abrasion, impact, flexibility, hardness, corrosion resistance and cathodic protection, and adhesion.

Some of these coatings require a certain degree of temperature control to cure properly, while others require heaters within the paint delivery line. With some paints, humidity is the crucial factor. Specialized application equipment is required for those coatings which are solvent-free, while other paints are potentially toxic to the persons applying them.

According to the California Air Resources Board (CARB), a survey conducted by them indicated that approximately 26 percent of the marine coatings sold in California were based on epoxy resins. Half of these coatings were based on amine-cured resins, and the remaining half were polyamide cured epoxies. Data from the CARB survey yielded that all the

TABLE 15-1

MARINE COATINGS: TYPES, APPLICATIONS, AND SOLIDS CONTENTS

Generic type	Percent Solids by Volume (Actual Range as Applied)		
	Primer	Intermediate Coating	Topcoat
Epoxy Amine	--	45-82	--
Epoxy Polyamide	28-50	45-65	35-55
Polyurethane	40-70	40-70	40-55
Vinyl	10-40	26-35	26-35
Chlorinated Rubber	20-35	30-36	34-40
Alkyd	14-50	14-50	14-50
Inorganic Zinc	38-62	38-62	38-62
Acrylic	23-30	23-30	25-35

Reference 1.

amine-cured epoxies sold in the state exceeded the required 55 percent solids recommended by the CARB and that 88 percent of the polyamide cured epoxies either meet or exceed the 50 percent solids level. According to paint manufacturers, the 55 percent solids level set for epoxy coatings (by CARB) can be achieved by the mid-eighties.

Chlorinated rubber coatings have gained wide acceptance in the marine industry and according to the same aforementioned survey, 82,000 gallons of chlorinated rubber coatings were sold in 1976. Approximately 90 percent of the coatings meet the proposed 35 percent solids level of the CARB rule.

Polyurethane coatings, with their high gloss and durability, are expected to meet the constraints of the CARB.

Acrylic coatings offer excellent protection against chalking and discoloration because of their resistance to ultraviolet radiation. The CARB did not expand on solids information in this coating category.

Of the vinyl coatings, approximately 45 percent comply with CARB rule recommendations. The vinyl coatings are used primarily by the Navy and since the Navy paint specifications require only a 20 percent solids level, considerable effort on the part of the Navy would have to be made if a rule such as the CARB's were to be put into effect.

At least three paint manufacturers market waterborne inorganic zinc primers which meet solids levels of the proposed CARB ruling1).

Table 15-2 presents a summary of marine coating sales and the resultant emissions in California. The proposed rule of the CARB is discussed in detail in the "Regulatory Status" section of this report.

CONTROL TECHNOLOGY

The use of low solvent coatings or of high performance coatings can achieve emission reductions from ship painting. The number of low solvent coatings which would be suitable for ships are rather

TABLE 15-2

SUMMARY OF MARINE COATING SALES AND RESULTANT EMISSIONS IN CALIFORNIA, 1976

Generic Type	1976 Sales (10^3 gal)	Emissions (tons/yr)
Alkyd	419	795
Epoxy	381	389
Chlorinated Rubber	82	174
Inorganic Zinc	67	121
Acrylic	64	119
Vinyls	55	149
Polyurethane	54	94
Other	30	83
Antifouling	163	265
Subtotal	1,314	2,188
Other Solvent	131	427
Total	1,446	2,615 tons/yr*

*10.5 tons/day, based on 250 days/year.

Reference 1.

limited. However, according to the CARB, the very low solvent coatings which were originally formulated for such applications as tank linings can be used on other areas of ships with a little modification.

Emission reductions can also be attained through the use of high performance coatings, even though they are not exceptionally low in solvent content. Due to the excellent physical durability, chemical resistance, and extended coating life of these high performance paints, less frequent recoating of the ship is required, thus resulting in reduced VOC emissions.

By incorporating the two control strategies, the use of low solvent (high solids) coatings, and the use of high performance coatings, the total VOC emission reduction in California would be to over 3.5 tons per day by 1985.

Conventional coatings are relatively low in solids content and generally fail in about one year. Examples of these types of conventional coatings include alkyds, modified alkyds, phenolic, and resin-base coatings. The high performance coatings can be high or low in solids content, but possess coating lives at least twice as long as those of conventional coatings. The high performance coatings include vinyls, chlorinated rubbers, modified acrylics, polyurethanes, and inorganic zincs. Table 15-3 presents both conventional and high performance coatings with cost and durability comparisons. By examining this table, it can be seen that though high performance coatings are more expensive than their conventional counterparts, the life of a high performance coating is sufficiently longer to yield greater cost efficiency.

Availability of High Performance Coatings

In preparation for the writing of this rule, the CARB surveyed numerous coating manufacturers and found that they all manufactured some coatings which would comply with the proposed model rule. This implys that no great economic hardship would be encountered by paint manufacturers as a result of air quality rulings.

TABLE 15-3

COMPARATIVE COSTS OF SIX COATINGS SYSTEMS (BASE YEAR 1976)

Type of System	Coats	Dry Mils	Cost ft^2/mil	Millage Cost	Total Cost $/$ft^2$.	Avg. Coating Life Expectancy*(yrs)	Cost $/$ft^2$/yr
A. Alkyd	2 Coats topcoat	2.5	.013	.033	.081	1	.081
Alkyd	2 Coats primer	3.0	.016	.048			
B. Chlorinated rubber	Topcoat	1.5	.017	.026	.136	2	.068
Chlorinated rubber	Intermediate	3.0	.018	.054			
Chlorinated rubber	Primer	3.0	.019	.056			
C. Epoxy polyamide	Topcoat	2.0	.015	.031	.123	4	.031
Epoxy polyamide	Intermediate	4.0	.015	.060			
Epoxy polyamide	Primer	2.0	.016	.032			
D. Polyurethane	Topcoat	1.25	.034	.043	.181	6	.030
High build epoxy	Intermediate	4.0	.012	.048			
Inorganic zinc	Primer	3.0	.030	.090			
E. Vinyl acrylic	Topcoat	1.5	.024	.036	.119	2	.060
Vinyl acrylic	2 Coats primer	4.0	.021	.083			
F. Vinyl acrylic	Topcoat	1.5	.024	.036	.174	2	.087
High build epoxy	Intermediate	4.0	.012	.048			
Inorganic zinc	Primer	3.0	.030	.090			

*Topcoat only.

Reference 1.

In the following section, the status of the regulatory activities will be discussed concerning primarily the CARB's "Proposed Model Rule for the Control of Volatile Organic Compounds from Marine Coatings Operations".

REGULATORY STATUS

The CARB in June 1978 proposed a rule entitled "Control of Volatile Organic Compounds from Marine Coatings Operations", which read as follows:

"1. After January 1, 1982, no person shall offer for sale or sell for use in this state or apply any marine coating which contains more than 295 grams of volatile organic compounds per liter of coating, excluding water.

2. Until January 1, 1985, the provisions of this rule shall not apply to the sale or application of:

   a. chlorinated rubber coatings containing less than 540 grams of volatile organic material per liter of coating, excluding water.

   b. Vinyl coatings containing less than 540 grams of volatile organic material per liter of coating, excluding water.

   c. Polyurethane coatings containing less than 420 grams of volatile organic material per liter of coating, excluding water.

   d. Epoxy coatings containing less than 380 grams of volatile organic material per liter of coating, excluding water.

3. The provisions of this rule shall not apply to:

   a. Antifouling coatings.

   b. Wash primers.

   c. Marine coatings sold in containers of one gallon or less."

This rule did not advance beyond the proposal stage since, according to a representative of CARB, the California shipyard owners made a strong case that business would be lost to out of state shipyards. The high performance, high solids coatings are more expensive than the conventional paints and apparently ship owners do not see enough advantage in using the more expensive paints even though they possess greater durability and have a longer potential life (as shown in Table 15-3)[2].

A similar comment was obtained from the South Coast Air Quality District (SCAQMD, Los Angeles Air Basin)[3]. A staff member explained that when the CARB dropped all activity concerning the marine coating rule, the SCAQMD attempted to promulgate a similar regulation; however, they also ran up against some similar obstacles. Further, the U.S. Navy was not prepared to accept the paint limitations in the proposed rule.

There is a unique quality to developing an emissions regulation for an industry such as ship coating, simply because the shipyards are in certain set locations, and ships, no matter where registered, are free to go from port to port and be painted at the most competitive prices. Ultimately, these shipyards in areas with air quality regulations requiring the use of high performance, high solids paints could be out of business by competitors whose yards are in regions with no regulations. The CARB and the SCAQMD feel the regulation should be applied at the federal level. However, since some shipyards are in attainment areas, and shipowners in some cases have the alternative of using foreign yards, the effect of Control Techniques Guidelines requirements would also be blunted.

REFERENCES

1. California Air Resources Board, Consideration of a Proposed Model Rule for the Control of Volatile Organic Compounds from Marine Coating Operations.

2. Phone discussion with staff member of the California Air Resources Board, February 1981.

3. Phone discussion with staff member of the South Coast Air Quality Management District, February 1981.

SECTION 16

SURFACE COATING OF WOOD FURNITURE

PROCESSES AND EMISSIONS

General discussion

The wood furniture industry which includes the products listed in Table 16-1 is the second largest source of VOC emissions among surface coating industries, due to the use of very high volumes of low solids coatings. Total nationwide volatile organic compound (VOC) emissions for 1973 from coatings used in this industry were 149,000 metric tons. In addition, approximately 83,000 metric tons of miscellaneous organic solvents were used for cleanup and thinning. Table 16-2 compares the emissions from wood furniture coatings which comprise over 10 percent of all industrial coating emissions, to other industry coating categories1).

Table 16-1 gives the structure of the wood furniture industry. There are six SIC codes (Standard Industrial Classification, U.S. Department of Commerce) which include those companies engaged in the manufacture of wood furniture. Table 16-3 presents the relative total number of establishments in each class. Table 16-4 gives the number of wood household furniture plants by EPA region2).

All wood furniture products are coated in a roughly similar way although furniture will usually receive a much more elaborate series of finishes during the coating process than kitchen cabinets.

Wood furniture, especially household, is generally categorized as being of three levels of quality: namely, high end, medium end, and low end. On a per unit basis, the relative percentages of each of these quality levels manufactured are 8, 28, and 64 percent respectively3). The quality of the furniture is determined in part by the number of coating operations performed on the piece. A low-end piece might typically undergo from three to six finishing operations, while a high-end piece of furniture could require 15 or more operations to obtain the desired finish. This is not universally true because some of the softer woods used in low-end furniture require additional finishing steps to achieve a satisfactory finish.

TABLE 16-1

WOOD FURNITURE INDUSTRY STRUCTURE

			Number of Establishments[1]				Number of Employees[1]			
SIC Code	Industry	Typical Products	Small	Medium	Large	Total	Small	Medium	Large	Total
2434	Wood Kitchen Cabinets	Cabinets, to be built-in Cabinets, factory made Vanities, bathroom and other	1,547	129	10	1,686	13,125	13,366	3,690	30,181
2511	Wood Household Furniture Except Upholstered	Beds, bookcases, buffets, chairs, chests, coffee tables, cradles, cribs, dressers, rockers, secretaries, stools, tables	1,444	307	116	1,867	17,214	34,649	64,522	116,385
2512	Wood Household Furniture, Upholstered	Chairs, couches, davenports, living room furniture, rockers, sofas	865	310	59	1,234	14,216	33,441	26,356	74,013
2517	Wood Television, Radios, Phonograph and Sewing Machine Cabinets	Phonograph cabinets and cases, radio cabinets and cases, sewing machine cabinets and cases, stereo cabinets, television cabinets	47	17	8	72	589	1,642	5,018	7,249
2521	Wood Office Furniture	Benches, bookcases, cabinets chairs, desks, filing boxes, furniture, stools, tables	186	46	9	241	2,605	5,187	3,834	11,626
2531	Public Building and Related Furniture	Benches, blackboards, bleachers, chairs, church furniture, seats	280	85	12	377	4,221	9,539	5,459	19,219
		TOTAL	4,369	894	214	5,477	51,970	97,824	108,879	258,673

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[1] By employment size: small = 1 to 49 employees; medium = 50 to 249 employees; large = 250 or more employees.

Source: County Business Patterns, 1975.

TABLE 16-2

VOC EMISSIONS FROM INDUSTRIAL COATINGS

Industry	Estimated Emissions (1000 metric tons/yr.)
Wood Furniture	230
Large Appliances	42
Magnet Wire	10
Automobiles	140
Cans	130
Metal Coils	30
Paper	390
Fabric	100
Metal Furniture	90
Flat Wood Products	84
Other Metal Products	230
Others	310
TOTAL	1,786

TABLE 16-3

WOOD FURNITURE CATEGORIES

SIC Code	Percentage of Total Facilities*
2434 - Wood Kitchen Cabinets	31
2511 - Wood Household Furniture, Except Upholstered	34
2512 - Wood Household Furniture, Upholstered	23
2517 - Wood Television, Radios, Phonograph and Sewing Machine Cabinets	1
2521 - Wood Office Furniture	4
2531 - Public Building and Related Furniture	7
TOTAL	100

*Based on 5,477 establishments for the six SIC codes.

TABLE 16-4

WOOD HOUSEHOLD FURNITURE PLANTS BY EPA REGION
(no data available for States not listed)

	Total Plants	Plants with 20 Employees or More
Region I		
New Hampshire	19	13
Massachusetts	90	29
Connecticut	21	5
Region II		
New York	258	59
New Jersey	69	18
Region III		
Pennsylvania	107	43
Maryland	16	4
Virginia	55	42
Region IV		
North Carolina	153	103
South Carolina	20	9
Tennessee	81	26
Kentucky	28	8
Mississippi	28	10
Alabama	59	18
Georgia	92	30
Florida	165	28
Region V		
Ohio	51	18
Indiana	75	43
Michigan	62	31
Illinois	81	31
Wisconsin	26	16
Region VI		
Texas	81	23
Louisiana	13	2
Arkansas	38	18
Oklahoma	21	4
Region VII		
Iowa	10	5
Missouri	33	14
Region IX		
California	369	111
Arizona	22	5
Region X		
Washington	34	10
Oregon	31	9

Processes

The wood furniture finish is applied in series of steps. There is a great variety in the number and complexity of coating steps that may be applied, but the basic ones and their purpose are as follows:

Finish	Purpose
Body Stain	Gives color uniformity. Develops wood grain and character.
Wash Coat	Seals wood surface; prevents subsequent unwanted staining from filler coat. Stiffens the wood fiber for subsequent sanding.
Filler	Fills large pores of wood.
Sealer	Seals the wood for application of subsequent coats.
Glaze, shading stains, padding, spatter	Small amounts of color coating that are added to highlight and give character to the wood. These are often hand wiped.
Topcoat	Usually nitrocellulose lacquer. Provides clear, durable final finish.

Table 16-5 gives a typical wood furniture schedule. Notice the number of persons required to perform each step. Wood furniture coating is a very labor-intensive industry and much of the labor force is unskilled. This dependency on large amounts of relatively unskilled labor is one reason the furniture industry may have difficulty adopting new technology. Furniture finishing is still something of an art and the techniques, equipment, and procedures may vary considerably from plant to plant.

In larger furniture factories, furniture pieces are loaded onto a conveyor line. Workers stationed along the line perform specific finishing operations as the furniture piece is carried by on the conveyor. The various coatings are usually applied by air spray although dip coating is sometimes used. There is usually a separate spray booth for each of the coating operations and typically one to three spray gun

TABLE 16-5

TYPICAL WOOD FURNITURE FINISHING SCHEDULE

Operation Number	Operation Name	Operation Time Allowed in Minutes	No. of Persons Per Operation
1	Load	5	1
2	Spray uniform stain	1.5	2
3	Dry	15	
4	Spray NGR stain	1.5	2
5	Dry	20	
6	Spray washcoat	1.5	2
7	Dry	20	
8	Sand lightly	1.5	4
9	Spray filler	1.5	2
10	Flash-off filler	2	
11	Wipe filler	4	8
12	Dry	45	
13	Spray sealer	1.5	2
14	Dry	30	
15	Sand	3	7
16	Spray sealer	1.5	2
17	Dry	30	
18	Sand	3	7
19	Spray glaze	1.5	2
20	Wipe and brush	5	13
21	Dry	60	
22	Distress	2	4
23	Spray lacquer	1.5	2
24	Dry	45	
25	Spray lacquer	1.5	2
26	Dry	75	
27	Unload	5	1
28	Return to load	15	
	TOTAL	399	63

Source: Technical paper, Society of Manufacturing Engineers, MS 75-251 operators are in each spray booth. After the furniture piece is sprayed, the conveyor carries it either to an oven or to the next spray booth. If the piece travels from spray booth to spray booth, it air dries. Sometimes there is an oven after a spray booth to give quicker drying. The wood cannot be heated above approximately 130°F, however, because at higher temperatures the natural moisture in the wood may be driven out and damage the coating. (The actual oven temperature may be somewhat higher than 130°F since the furniture piece does not remain in the oven very long.) The oven is used mainly to flash-off and dry solvent since the oven temperature is not hot enough to bake or cure the coating. Oven drying may be used after any of the coating operations. The finishing step on which ovens are actually used varies widely from plant to plant. Sometimes ovens are not turned on in the summer when the temperature in the finishing room is high.

The coating operation may include various glazes, shading stains, wiping stains, and padding stains which are usually added between the sealer and topcoat, but may be added elsewhere as there is a great deal of variation in furniture schedules. These glazes and shading stains are usually sprayed on and then hand wiped to give a special appearance to certain parts of the furniture such as edges and corners. The more expensive pieces of furniture usually have more of this hand-type rubbing work. Hand wiping may also be used after other coating operations such as application of the body stain.

Types of Emissions

As stated in Table 16-2, annual VOC emissions from wood furniture coatings are estimated at 230,000 metric tons per year. Individual furniture factories vary greatly in size, but a moderately large factory can emit around 1300 kilograms of solvent per day or over 300 metric tons per year. These emissions are almost totally from coatings used to finish the furniture. The amount of solvent emissions from a piece of furniture depends on the amount of each type of coating used as well as its solvent content. although this will vary, Table 16-6 gives the approximate relative emissions from different coatings in a coating system for a specific line of furniture. Conventional coatings often

TABLE 16-6

RELATIVE EMISSIONS FROM A TYPICAL CONVENTIONAL FURNITURE COATING SYSTEM

Finish	lbs. VOC/1000 ft^2	Percent of Total
Stain	26	12
Washcoat	38	18
Wipe Stain	24	11
Sealer	36	17
Glaze	25	11
Fly Speck	0	0
Cowtail	0	0
Shade	10	5
1st Topcoat	29	13
2nd Topcoat	29	13
	216	100%

consist of nitrocellulose resins and organic solvents. The approximate solids content of furniture coatings are given in Table 16-7.

The stain emissions listed in Table 16-6 are from an organic solvent-borne stain. There are various types of stains; one of the most common is organic-borne NGR (nongrain raising) stain. It is composed of a dye in an organic solvent. it dries rapidly and does not raise the grain very much. Waterborne stains also exist and have been used for many years.

More solvent comes from the topcoat than from any other step in the coating system. Usually two or three coats of topcoat are applied. More than 85 percent of topcoats now used are nitrocellulose lacquers. These have been used for over 30 years and are well accepted by the industry. Nitrocellulose lacquer has many desirable properties of which one of the most important is the excellent appearance of the finish.

About 15 percent of topcoat materials are other synthetic organic resins such as urea formaldehyde and catalyzed urethane finishes. They are very durable and are used on cheaper furniture and on institutional furniture where heavy use is expected.

The organic solvent content of coatings is the main interest to an air pollution control agency. The typical solvent types employed in wood furniture coatings are:

Acetone
Acetates
Alcohols
Aromatic hydrocarbons
Esthers
Glycol ethers
Ketones
Mineral spirits

CONTROL TECHNOLOGY

General Discussion

Volatile organic carbon emissions from wood furniture finishing operations can be reduced by changes in materials or processes, and/or by the application of add-on emission control devices. Material changes

TABLE 16-7

APPROXIMATE SOLID CONTENT OF WOOD FURNITURE FINISHES

Finish	Percent Solids by Volume
Body Stain	1
Washcoat	8
Filler	40
Sealer	14
Glaze	24
Topcoat	14

involve reduction in the quantity of VOC components in the coating. One approach is the use of waterborne coatings in place of organic solvent-borne coatings. Another alternative involves increasing the solids/solvent ratio in the coating as applied.

Operational changes are directed towards reducing the quantity of wasted coating. This is material which does not actually get applied to the product but, for example, in the case of a sprayed coating, is exhausted from the booth to the atmosphere. The ratio of coating adhering to the substrate to the coating used is defined as "transfer efficiency".

Permanent or add-on controls for VOC emissions in the furniture industry have not traditionally been used. Incineration would be the most likely approach and could be considered as technologically feasible.

Waterborne Coatings

Waterborne coatings include all those coatings in which all or most of the volatile (or non-solids) portion of the formulation consists of water instead of organic solvents. Such coating materials have been manufactured for a number of years and are used on metal products, particularly electrodeposited prime coats, baked pigmented top coats, trade sales for painting of wood, and especially for architectural surfaces such as walls and floors. In the case of wood furniture manufacturing, coatings have been available for a short period of time. In 1974, the Reliance Chemical Company displayed waterborne coated furniture at the Louisville Furniture Supply Fair4). The stain, sealer, glaze, and clear topcoat were entirely waterborne formulations. Other paint companies have also displayed waterborne coated furniture at Louisville.

Additionally, the U.S. EPA sponsored a display of waterborne coated wood furniture at the Southern Furniture Manufacturing Association show in High Point, North Carolina in 1979. This furniture was observed by both manufacturers and visitors. There was no definitive consensus on the visual appearance of the furniture. There were both positive and negative reactions, as might be expected with such a subjective rating factor as appearance.

European companies also produce waterborne coatings for wood furniture. In 1976 a Swedish company introduced a waterborne system consisting of stains and lacquers for both light and dark wood surfaces[5]. This company reports that drying times are less than for many conventional lacquers.

There are a limited number of manufacturers who are using complete waterborne coating systems for furniture, including case work and office furniture manufacturers. Some use waterborne topcoats, while waterborne body stains have been used in the industry for several decades and are fairly well established in the furniture industry.

The topcoat is generally considered to be one of the more difficult coats to formulate as a waterborne coating. In part this is due to the problem of achieving the desirable gloss, clarity, and surface sheen with waterborne clear topcoats as compared to the industry standard of solvent based nitrocellulose lacquers. Also, the furniture industry produces a wide product mix ranging from simple box-like cases through open work chairs, to complex and ornate large cabinets and tables. The lack of a standard product and the subjectivity in judging acceptable appearance probably are major factors in the slow acceptance of waterborne coatings[6].

Several recent articles in the trade literature discuss waterborne coatings for wood furniture[7,8,9]. These articles recognize that there are problems, but take an optimistic view of the waterborne coatings for wood furniture.

Below are some general comments on the characteristics of waterborne coatings for several properties important in wood furniture coatings.

1. The appearance of waterborne coatings can differ in some respects from solvent-borne coatings according to industry critics. The most important differences relate to gloss and clarity. Waterborne finishes can have less luster and color depth. The average person may not see these differences as acutely as would a furniture specialist.

2. The repairability of coatings is reportedly not as good with waterbornes since repair coats do not blend as well with previous waterborne coats. Roughly 10 to 20 percent of wood furniture must undergo refinishing at the manufacturing site. Waterborne coatings can be repaired at the dealer by using conventional solvent-borne touch-up coatings. Roughly 10 percent of furniture which reaches the dealer has to undergo repair due to abrasion of finish during shipping.

3. Ease of application is somewhat controversial. It has been reported that "certain waterborne emulsions can be formulated to air spray and dry in a manner virtually identical to conventional lacquers"7). Other coating suppliers have stated that waterborne coatings do not dry as quickly as solvent coatings. At any rate, dry tme does not appear to be a major problem. Waterborne stains are currently being applied on conventional coating lines.

   Another problem is the difficulty with which the paint is applied. Some furniture manufacturers state that in experimental runs, sprayers have more difficulty in applying the paint evenly and have more rejects. This problem can probably be corrected as the spray gun operators get more experience with waterborne systems.

   Although waterborne coatings are more sensitive to variations of humidity and temperature during application than conventional coatings, they are known to be applied to other substrates under a variety of these conditions. High humidity is also a problem with conventional solvent coatings due to solvent "blushing" where the solvent picks up moisture and causes a clear coating to turn white.

4. Compatibility with previous layers of coating, although reportedly not as good as with waterborne coatings, is acceptable.

5. Mar resistance or "print resistance" (resistance to blemishes caused by pressure on the coated surface) is somewhat of a

problem when fast line speeds and minimum oven heat are used. Some furniture makers store pieces of furniture stacked on top of each other in the warehouse and are afraid this will be a problem if waterborne coatings are used.

6. Water and alcohol resistance are acceptable. Although there is limited field data, waterborne furniture appears to be as tough as solvent coated furniture in standing up to household wear.

7. Waterborne topcoats have more difficult polishing or "rubbing" characteristics than nitrocellulose topcoats. New rubbing techniques will have to be developed.

In summary, according to furniture makers, the main problems with waterborne coatings (especially topcoats) are "clarity", "rubbing" characteristics, and print resistance. Also, training of workers to apply the coatings may be a short-term problem.

There are several operational aspects relating to the use of waterborne coatings that should be recognized. The most important are given below.

It is generally agreed that flash-off areas may have to be extended to allow proper flash-off of the water. Similarly, curing ovens may have to be modified to drive the water out of the finish, potentially increasing energy costs. Additionally, there could be a requirement for humidity control.

Corrosion of the bulk storage system can occur with waterborne finishes but can be avoided by replacing lines, pump materials, and spray gun fittings with stainless steel units and by lining the inside of storage vessels. This will require additional capital expenditures. Freezing of the waterborne finishes is also a major concern since most furniture manufacturers store their conventional solvent-borne finishes outdoors because of fire hazards. Inside storage of waterborne finishes may be required. (Fire hazards are reduced with waterborne finishes.)

Emissions reduction potential by the use of waterborne coatings can best be expressed as a range. Reductions obtained in the trial program sponsored by EPA ranged from 26 to 94 percent. Replacing wash coat and sealer with waterborne substitutes resulted in a 26 percent emission reduction, while a 30 percent reduction was obtained by converting color coats to waterborne and retaining conventional clear coats. Totally converted finishes yielded up to 94 percent emission reduction. Reductions expressed as a percentage are, of course, sensitive to the original amount of VOC emissions from solvent-borne systems. In the case of the EPA trials emission levels from the standard systems used ranged from about 85 kg per 100 m^2 of surface covered to 160 kg per 100 m^2.

Electrostatic Coating Application

The conventional method for applying surface coatings to wood furniture is with an air atomizing spray gun. In most cases these guns are hand-held. The transfer efficiency with these systems is usually less than 50 percent. It can be greater with large solid objects and can be considerably less with smaller items such as open work chairs, chair legs, spindles, and small panels. This poor transfer efficiency is the result of both overspray and bounceback.

Electrostatic coating is based upon the principle that opposite electrical charges attract each other. Since the atomized coating particles are negatively charged by the application device, the article to be coated must be positively charged or grounded. Transfer efficiencies with electrostatic equipment typically can be improved to 65 percent, and under optimal conditions, using automated bell and disk systems together with conveyorized parts, can reach 85 to 95 percent10).

Several types of atomizing devices are used with electrostatic application systems. These include rotating disk and bell units where atomization is produced by centrifugal forces, air atomizing hand guns, and airless (hydraulic) spray guns. Disk or bell atomizers are most often used in automated systems where the atomizer is mounted on a reciprocater which moves up and down. The parts are held on a conveyor which transports them past the atomizer in a loop pattern. As the parts pass along the loop they are rotated or indexed to maximize exposure to the spray pattern.

As mentioned earlier, the objects to be electrostatically coated must be positively charged or grounded. Because wood (particularly when dry) is not conductive, it must be treated with a sensitizing material. These conductive chemicals are applied in a very thin layer by spraying, dipping, or flow coating. The coating is transparent and does not interfere with or detract from subsequent coating steps. Following application of the sensitizer, the object to be coated must be passed through a humidification booth or similar chamber where it is exposed to an atmosphere of about 50 percent relative humidity for approximately one minute(11). Following this treatment objects to be coated can easily be grounded if they are transported through the coating process on a metal conveyor. In the situation where objects are pallet-mounted (generally larger case goods) individually devised grounding techniques must be utilized.

A fairly modest improvement in transfer efficiency can result in significant reduction in VOC emissions. As an example, an improvement from 40 to 60 percent in transfer efficiency is equivalent to nearly 47 percent reduction in VOC emissions.

Add-On controls (Incineration)

Incinerators have been rather widely used control VOC emissions at the point of discharge to atmosphere. In most such cases, however, they have been used in conjunction with unmanned operations such as gasoline storage and transfer, asphalt air blowing, can and coil coating, automotive surface coating, and resin cooking where VOC concentrations are fairly high. In the case of fume incinerators serving baking or drying ovens, heat recovery has been successfully applied. Considering the cost of fuel, other opportunities for heat recovery are constantly being explored. In principle, fume incineration should be technologically feasible for destruction of VOC emissions from furniture coating as the actual design of hooding, ducting, and incinerators does not require new design principles.

At the present time there are no known fume incinerators used in conjunction with wood furniture coating in the United States. Cost, absence of regulations, and safety considerations have a bearing in this situation. A substantial portion of the VOC emissions from wood furniture coating arises from manual spraying operations where ventilation rates must meet OSHA standards. This generally results in rather dilute VOC concentrations in the spray booth exhaust and therefore a relatively larger volume of exhaust air per unit of VOC emissions than in many systems where fume incinerators are used. Also, there can be relatively large numers of potential emissions points per plant because of the multiple operations performed. While these sources could be manifolded together, there has been concern in the industry about the fire risk from overspray deposits of highly flammable nitrocellulose resins in long exhaust ducts.

It is possible that incinerators could be selectively applied as part of an overall control strategy using some of the following criteria:

1. Apply incinerators only to fairly high concentration streams such as drying ovens, flash-off areas, or automated booths.
2. Avoid nitrocellulose buildup problems by either (a) restricting application to non-spray booth uses, or (b) removing particulate nitrocellulose with filters or water wash prior to entry into ductwork.
3. Use fire control systems such as water deluge, inert gas blanketing, etc.

Where incinerators are used, control efficiencies of at least 90 percent can be attained on VOC emissions reaching the incinerator.

STATUS OF REGULATORY ACTIVITIES

Existing rules and regulations at the state and local level are all generic rather than being directed specifically at surface coating of wood furniture. An example is Rule 442 of the South Coast Air Quality Management District, California, covering the usage of solvents.

This rule generally restricts solvent emissions by requiring an 85 percent reduction in emissions or by limiting daily and/or hourly emission rates. The general limitation for emission of non-photochemically reactive solvents is 272 kilograms (600 pounds) per day, effective December 1, 1980. Organic materials which come into contact with flame or are baked, heat cured, or polymerized are limited to 6.5 kilograms (14.3 pounds) per day. Emissions of photochemically reactive solvents are limited to 14 kilograms (3.1 pounds) per hour, not to exceed 18 kilograms (39.6 pounds) per day. Information obtained from a District spokesman indicates that none of the wood furniture coating operations within their jurisdiction have elected to use add-on controls to achieve compliance with the rule12). Instead, they operate within the hourly and daily limits on emissions by limiting solvent use and by solvent substitution (for photochemically reactive solvents originally used). At least one plant manufacturing chairs has made a partial conversion to waterborne coatings. Under the agenda of the California Suggested Control Measures Committee, the South Coast Air Quality Management District is taking the lead to develop a Model Rule for the Surface Coating of Wood Furniture. This rule may be considered during the year 1981. At the present time emphasis is on developing a rule to require improved transfer efficiency such as with airless or electrostatic spray equipmnt. However, a decision on the exact content or numerical standards has not yet been reached13).

A major consideration will be the form of an industry specific rule. Most rules applying to other industries have been based upon an equivalent limit on organic solvents per quantity of coating (less water) as applied. This is a possibility for the wood furniture coating industry, but there is great variability in the number of coatings applied and the solvent content of the these coatings depending upon the type of product and the manufacturer. A more uniform limit could be based upon the amount of VOC emissions emitted per unit area coated, such as kilograms VOC per 100 m^2 of surface coated. This latter approach would probably involve a more involved compliance checking procedure.

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13. Personal communication between R. J. Bryan, Engineering-Science, Inc., and A. Rawulka, South Coast Air Quality Management District, March 16, 1981.

SECTION 17

WASTE SOLVENT RECOVERY INDUSTRY

Organic solvents used by industries for extractions, for cleaning, and as chemical mediums or intermediates are available as halogenated, aliphatic, and aromatic hydrocarbons; as alcohols, esters, glycol ethers, ketones, and nitroparaffins; and as miscellaneous compounds such as tetrahydrofuran. These classifications include methyl ethyl ketone, benzene, perchloroethylene, and isopropanol.

A solvent not consumed during industrial use usually becomes contaminated and unacceptable for further use. A reclaimed solvent can be reused for its original purpose or for different industrial needs. Reclaiming waste solvents has gained importance because the costs of these petroleum derivatives are dependent on the cost of crude oil. Furthermore, the rising costs of virgin solvents and waste solvent disposal have provided incentives for industries to recover solvents for reuse.1)

PROCESSES AND EMISSIONS

The waste solvent recovery industry is composed primarily of small plants using straightforward chemical-processing technology. Typically, a single plant has an analytical laboratory, a distillation device, and storage tanks. The usual flow through the plant follows the diagram in Figure 17-1: the solvent-bearing material entering the plant is analyzed in the lab, pumped into cone-bottom separation tanks where heavy solids and water settle out, and put through a flash distillation device which is typically a thin-film evaporator. For most plants, this is the end of the recovery process.

The composition of materials handled varies widely in vapor pressure and type of solvent. A list of solvents most frequently recovered appears in Table 17-1. This clean solvent-blend product usually goes to storage for later sale or for return to the contracting company, and the sludge is disposed of by sending it either to an incinerator or to a landfill.

FIGURE 17-1

SIMPLIFIED FLOW PATTERN THROUGH TYPICAL SOLVENT RECOVERY PLANT

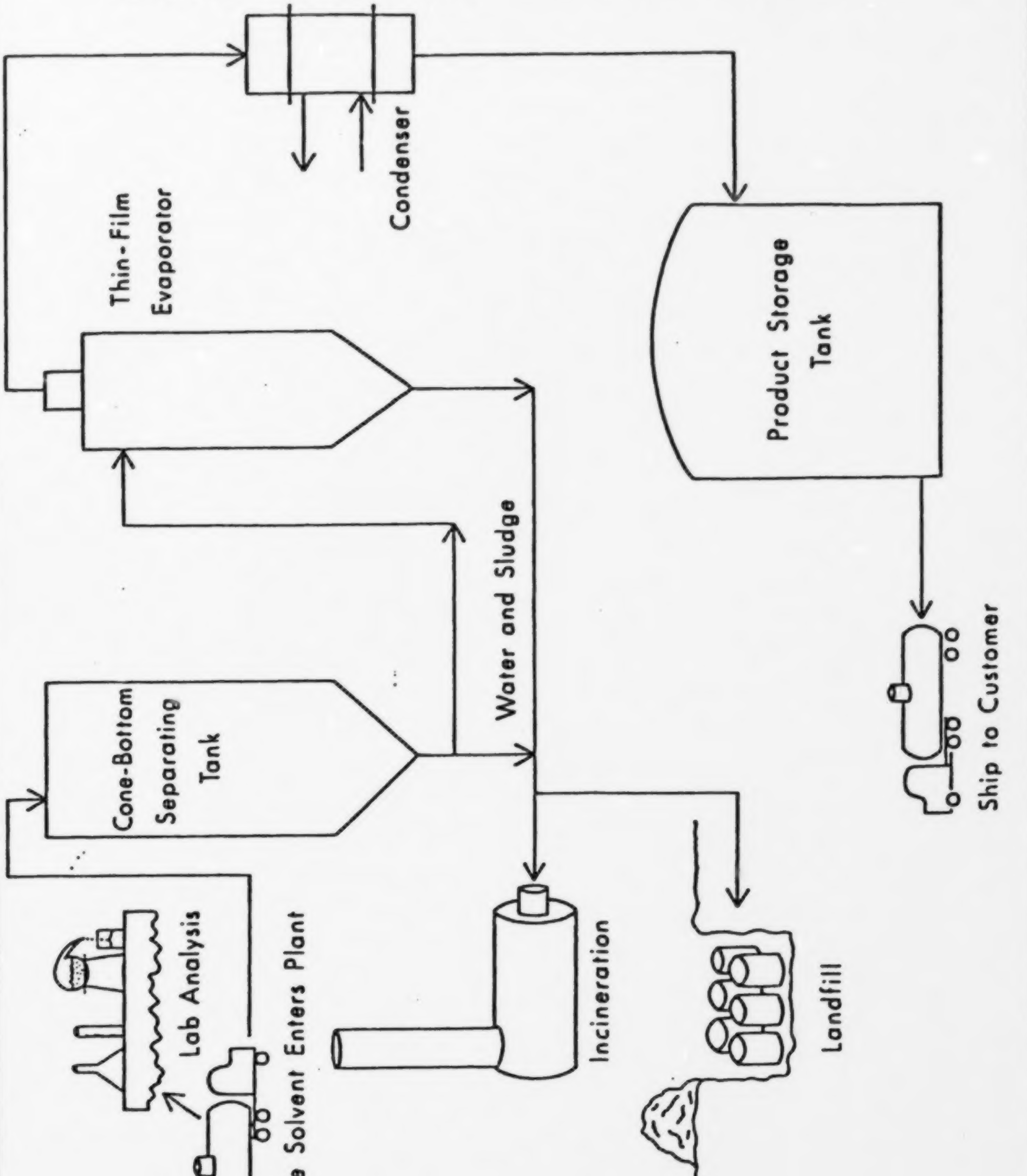
Waste Solvent Enters Plant
Lab Analysis
Cone-Bottom Separating Tank
Thin-Film Evaporator
Condenser
Water and Sludge
Incineration
Landfill
Product Storage Tank
Ship to Customer

TABLE 17-1

TYPICAL SOLVENTS RECOVERED

Solvent	Vapor Pressure PSIA @ 68°F
Halogenated Hydrocarbons	
Carbon tetrachloride	1.5
Fluorocarbons	-
Methylene chloride	6.8
Perchloroethylene	0.2
Trichloroethylene	0.9
1,1,1-Trichloroethane	1.6
Hydrocarbons	
Hexane	1.9
Benzene	4.4
Toluene	0.3
Xylene	0.1
Cyclohexane	1.5
Ethers	7.0
Mineral spirits	-
Napthas	1.3
Ketones	
Acetone	2.9
Methyl ethyl ketone	1.2
Methyl isobutyl ketone	0.2
Cyclohexanone	9.4
Alcohols	
Methanol	1.5
Ethanol	0.9
Isopropanol	0.5
Butyl alcohol	0.2
Amyl alcohol	-
Esters	
Amyl, butyl, ethyl acetates	-

Some large plants are capable of separating the clean solvent blend into two or more components, usually by using a fractionating column with a center-feed and with overhead and bottom-product takeoffs. Plants with high-technology recyclers have large multistage columns capable of reclaiming solvents with a high degree of purity, but the throughput of these plants is usually limited to a specific industry.

Storage tanks are the largest source of emissions. Typically, plants have a relatively large number of small tanks, ranging from 1000 to 20,000 gallons; many have a few tanks outside this range. Most tanks are fixed roof, straight sided, and erected vertically above ground; however, some horizontal tanks are in use primarily as receivers.

Emissions from storage tanks are from working losses and breathing losses. Working loss emissions come from filling an empty tank with material that pushes the organic vapors within the tank out through vents or open hatches to the ambient air. If a residue remains in a tank after previous unloading, concentrations of VOC's are often near saturation. Breathing loss emissions come from an inactive partially filled tank being exposed to temperature differences between day and night; as the tank heats up, inactivity allows the material to saturate the air with vapor, so the saturated air expands and vents to the ambient air.2)

Other points of emissions are fugitive sources such as pump seals, valves, flanges, and spills. Spills occur when connections are uncoupled and opened because residual material remains at the coupling. Other spills are due to line ruptures, tank overflowing, and plugged-line repairs.

The amount of emissions from waste solvent recovery plants is small. Emissions for a large plant with an annual throughput of 2.5 million gallons are less than 60 tons per year. Emission factors for solvent-recycling facilities are in Table 17-2.

CONTROL TECHNOLOGY AND ASSOCIATED COSTS

Few control options are available to recyclers. For control of emissions from storage tanks, an internal floating roof with primary

TABLE 17-2

EMISSION FACTORS FOR SOLVENT RECLAIMING

Source	Criteria Pollutant	Emission Factor Average*	
		lb/ton	kg/Mg
Storage tank vent	Volatile organics	0.02 (0.004-0.09)	0.01 (0.002-0.04)
Condenser vent	Volatile organics	3.30 (0.52-8.34)	1.65 (0.26-4.17)
Incinerator stack	Volatile organics	0.02	0.01
Incinerator stack	Particulates	1.44 (1.1-2.0)	0.72 (0.55-1.0)
Fugitive emissions			
Spillage	Volatile organics	0.20	0.10
Loading	Volatile organics	0.72 (0.00024-1.42)	0.36 (0.00012-0.71)
Leaks	Volatile organics	NA	NA
Open Sources	Volatile organics	NA	NA

*NA - Not Available.

Source: Compilation of Air Pollutant Emission Factors, 3rd edition, including Supplements 1-10, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, AP-42, August 1977.

seals is available, but it would require fairly expensive retrofits of all existing vertical-side tanks. Capital costs would start at $24,000 per tank, and increase with size. At $1.2 million per megagram ($1.1 million per ton) of emissions$^{3)}$, this option would not be cost effective.

Emissions from fugitive sources are best controlled by monitoring and maintenance. This option would require two workers to go through the plant periodically with a portable hydrocarbon detection device to determine if there are leaks, and if so, where and how much. At a designated cut-off level, the offending component would either be repaired or replaced. Although not as expensive as the tank retrofit, there would be large expenditures required for two detectors, one for use and one spare; two workers for proper monitoring; an inventory of spare parts and replacement equipment; and an allotment of labor time for indicated repairs. The overall cost effectiveness would be about $2000 per megagram ($1818 per ton) of emissions.$^{4)}$

REGULATORY STATUS

Currently, no air pollution regulations exist that specifically pertain to the waste solvent recovery industry. There are many general VOC emission rules that may apply to specific processes.

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SECTION 18

WINE MAKING

PROCESSES AND EMISSIONS

Wine is made by the controlled fermentation of the juice of certain fruits, chiefly grapes. During the fermentation the natural sugar content of the fruit is converted into ethanol by the reaction:

$$\underset{\text{(sugar)}}{C_6H_{12}O_2} \qquad \underset{\text{(ethanol)}}{2C_2H_5OH} \qquad + 2CO_2$$

This process takes place in the presence of specially cultured yeast.

The final alcohol content of natural wines ranges from about 7 to 14 percent, depending upon the original sugar content of the grapes. A typical sugar content is about 20 percent. Theoretically, the yield of ethanol should be 51.1 percent by weight of the initial sugar content. The actual yield is found to be around 47 percent. The remaining sugar is lost as alcohol or byproducts of complex chemical mechanisms, or it remains in the wine as the result of incomplete fermentation.

While the basic elements of wine making appear to be relatively simple and straightforward, there are significant numbers of variables which are closely controlled by modern wineries, depending upon the type of wine being produced. A number of these variables influence the quantity of alcohol which could possibly be lost to the atmosphere. Among the most important are:

(1) Initial Sugar Content of Fermenting Material - As seen from the chemical equation for alcohol fermentation from sugar, the theoretical alcohol content of the wine varies directly with the amount of sugar present. Furthermore, the amount of gaseous carbon dioxide formed also increases with sugar content. Increases in alcohol content and rate of carbon dioxide evolution both increase the potential for alcohol loss to atmosphere.

(2) Nature of Fermentation Material - Red wine is fermented from crushed black or red grapes where of all the solid material, only a portion of the stems are removed. This mixture of skins, pulp, other solids, and juice is termed "must". White wine is fermented from juice extracted from crushed or macerated grapes. Limited testing by wine manufacturers and research organizations have shown slightly higher alcohol losses from must as compared to juice fermentation1). the reason for this is not known.

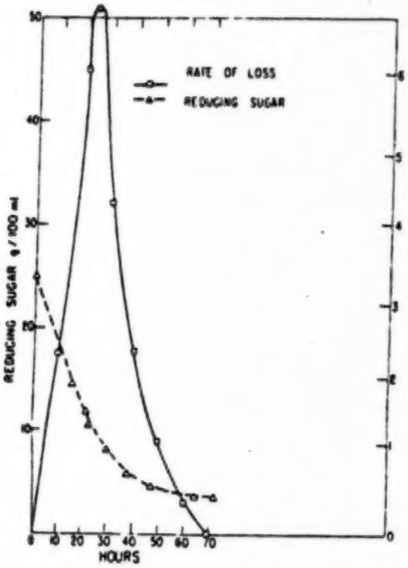
(3) Temperature of Fermentation - Wine is fermented at temperatures ranging from about 11°C to 30°C. White wines are fermented at the lower temperature ranges, while red wines are fermented at higher temperatures. Heat is generated during the fermentation which must be removed through use of cooling coils. Both laboratory and wine cellar fermentation tests have shown higher alcohol losses at higher fermentation temperatures. Figures 18-1 and 18-2 demonstrate this relationship for controlled laboratory fermentations.

(4) Agitation - During fermentation the fermenting mixture is internally mixed or air blown under certain circumstances. Limited testing shows instantaneous increases in alcohol los during and immediately following such agitation1).

When the fermentation is complete, the wine goes through a finishing process for clarification. Common clarification procedures are filtration, fining refrigeration, pasteurization, and aging. The wine is then bottled, corked or capped, labeled, and cased. Little is known about the loss of alcohol during the post-fermentation stages of wine production.

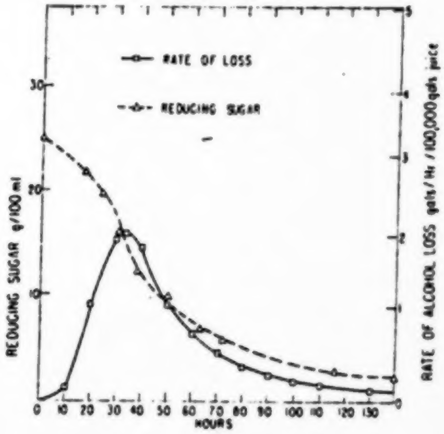
Emission estimates of typical alcohol losses during fermentation have been made as a result of limited laboratory scale and field testing. These losses have been expressed in terms of the fraction of the total theoretical alcohol available and as an emission factor in terms of

FIGURE 18-1 1)



Rate of loss of alcohol entrained in carbon dioxide during stirred laboratory scale fermentation with temperature maintained at 34°C.

FIGURE 18-2



Rate of loss of alcohol entrained in carbon dioxide during stirred laboratory scale fermentation with temperature maintained at 21°C.

weight of alcohol lost per unit volume of fermenting material. Zimmerman, et al[1], reports alcohol losses ranging from about 0.1 to 1.5 percent of total alcohol available. The smaller losses are associated with low fermentation temperatures (5 to 10°C) and a lower range of initial sugar content (10 to 20 percent by weight of fermenting material).

Emission factors reported in AP-42[2] are given in terms of grams of alcohol lost per kiloliter of fermentation material and lb./1,000 gals. Typical losses for white wine are given as 125 g/kl (1.06 lb./1,000 gals.) at 11.1°C (52°F) to 574 g/kl (4.79 lb./1,000 gals.) at 26.7°C (80°F) and 20 percent initial sugar content. For red wine fermented from must, a supplemental factor of 288 g/kl (2.4 lbs./1,000 gals.) is added to the higher temperature figure. In addition, an empirical equation is given to calculate emission factors at other conditions. This equation is:

$$EF = [0.136T - 5.91] + [(B - 20.4)(T - 15.21)(0.00685)] + [C]$$

where

EF = emission factor, pounds of ethanol lost per 1,000 gals. of wine made

T = fermentation temperature, °F

B = initial sugar content, °Brix (percent by weight)

C = correction term, 0 (zero) for white wine or 2.4 lbs./1,000 gals. for red wine

A loss of 8.9 lbs./1,000 gals. is equivalent to a loss of 1 percent of total alcohol available. Thus the loss levels given by Zimmerman in percent terms are reasonably consistent with the emission factors given in AP-42.

CONTROL TECHNOLOGY

There are no regularly used commercial control devices applied in the wine industry to reduce alcohol losses as these losses are generally under 1 percent of the total alcohol produced, and presumably there has not been a sufficient economic incentive to do so. There has been some experimentation with control devices including scrubbers. No efficiency data were reported but alcohol recovery by the control apparatus in two different studies[3,4) was found to be about 1 percent of the total alcohol produced. Since this is equivalent to the higher loss levels reported, it would appear that the control devices were reasonably efficient.

Conceivably, refrigeration, adsorption, or absorption (scrubber) type control devices could be used to capture alcohol emissions. These devices, to be fully effective, would have to provide a means of recovering and utilizing the alcohol collected. Further, the alcohol loss shows a rather sharp peak rate at about the middle of the fermentation period and is associated with significant carbon dioxide evolution. This would present a problem in design capacity of any proposed control system. If designed for peak rate of emissions, the capacity might be utilized for only a relatively small portion of the total fermentation period. Because there are no commercially used controls, control costs cannot be directly estimated. However, the scale of any such equipment can be roughly estimated. Because most of the alcohol losses are associated with the active evolution of carbon dioxide during fermentation, any control equipment would have to be sized to handle the volumetric flow rate CO_2. The fermentation reaction shows that there is about 49 lbs. of CO_2 evolved per 100 lbs. of sugar used. This is equivalent to roughly 7,500 ft^3 of CO_2 evolved per 1,000 gals. of fermenting material (20 percent initial sugar content). If the fermentation takes 250 hours, the CO_2 is evolved at an average rate of 30 ft^3 per hour. As seen by the laboratory experiments, the peak rate may be several times the average rate. For a peak rate three tmes the average rate and a 10,000 gal. fermentation tank, the peak CO_2 evolution rate would be about 15 ft^3 per minute. The ethanol content would be about 1 percent of this flow. Compared to many industrial pollution sources, this is a very low volumetric rate of gas discharge.

STATUS OF REGULATORY ACTIVITIES

Currently there are no regulations covering the discharge of ethanol to the atmosphere from wine making. A joint study currently is being conducted of possible ethanol losses from wineries by the Fresno County, California, Air Pollution Control District and the California Air Resources Board (CARB). Additional source testing and evaluation of control technologies are covered in the study plan. Depending upon the results of the study, it is possible that the CARB will propose a model rule.

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SECTION 19

STYRENE-BUTADIENE COPOLYMER LATEX

PROCESSES AND EMISSIONS

This chapter discusses the processes used in the manufacture of styrene-butadiene latex and the sources of volatile organic compound (VOC) emissions from these processes. The applicable emission control techniques are discussed, and a review of the air pollution regulations applicable to styrene-butadiene latex manufacturing is presented. Styrene-butadiene latex is defined as any latex polymer in which styrene and butadiene together comprise more than 85 percent by weight of the reacted monomer content, and butadiene alone comprises more than 15 percent by weight of the reacted monomer content. This definition would not cover polymers such as ABS (acrylonitrile-butadiene-styrene), in which all three monomers are present as a significant fraction of the total, but would cover latexes of styrene and butadiene which are modified with small amounts of vinylpyridine, acrylic acids, or other monomers.

Copolymers of styrene and butadiene can be made by a solution polymerization process or by an emulsion polymerization process. The solution polymerization products are sold as solid thermoplastic elastomers. The emulsion polymerization products can be sold in either a solid form, known as crumb, or in a liquid form, known as latex. The crumb product is used extensively in the manufacture of rubber tires, and has an average styrene content of 23.5 percent by weight.[1] The latex products have a wide variety of uses, depending on the styrene content of a particular grade. The rubbery types of approximately 23 percent styrene are used for dipped goods, carpet underlay, adhesives, and moldings. Small quantities of vinylpyridine monomer may be added if the latex is to be used for dipping tire cords. The high styrene latexes, ranging from 46 to 85 percent styrene, are used for paper coatings, paints, carpet backsizing, and adhesives. Small quantities of a carboxylic monomer, such as acrylic acid, are sometimes added to provide a "self-curing" material for use in carpet backsizing. Table 19-1 lists the U.S. producers of styrene-butadiene latex, the plant locations, and the capacities.

TABLE 19-1. DOMESTIC PRODUCERS OF STYRENE-BUTADIENE LATEX[2,3]

Company	Plant location	Annual capacity (10^3 Mg)
Dow Chemical Company	Bayport, TX Dalton, GA Gales Ferry, CT Midland, MI Pittsburg, CA	20
Firestone Plastics Company	Pottstown, PA	4
General Tire and Rubber Company	Mogadore, OH	47
BF Goodrich Company	Louisville, KY	NA[a]
Goodyear Tire and Rubber Company	Calhoun, GA	NA[a]
W.R. Grace and Company	Owensboro, KY	7
	South Acton, MA	7
Reichhold Chemicals, Inc.	Cheswold, DE	20
	Kensington, GA	25
Rubber Research Elastomers	Minneapolis, MN	NA[a]
Polysar Resins, Inc.	Chattanooga, TN	30
	Chattanooga, TN	30
	Beaver Valley, PA	20
Union Oil Company of California	Charlotte, NC	8
	La Mirada, CA	9
U.S. Steel Corporation	Scotts Bluff, LA	NA[a]

[a] NA = not available.

Process

As shown in the general flow diagram depicted in Figure 19-1, fresh styrene and butadiene are piped separately to the manufacturing plant from the storage area. The butadiene stream is passed through a caustic soda scrubber to remove any inhibitors that have been added to prevent premature polymerization during shipment and storage. Soap solution, activator, catalyst, and modifier are added to the monomer mixture prior to entering the polymerization reactor train. The soap solution is generally a mixture of a rosin acid soap and a fatty acid soap used to maintain the monomers in an aqueous emulsion state. The activator is usually a hydroperoxide or a peroxysulfate which initiates the polymerization reaction by supplying free radicals. The catalyst assists in generating the free radicals more rapidly and at lower temperatures than is possible with thermal decomposition of the activator alone. The modifier is an additive used to adjust the chain length and molecular weight distribution of the product during polymerization.

Most emulsion latex polymerization is done in a batch process, rather than continuously. The batch reaction is normally carried out at 50°C (122°F), and is taken essentially to completion (97 to 99 percent conversion). As a result, the recovery of unreacted monomers is not economical and the process is directed towards maximum conversion on a once-through basis. Some latex manufacturers (approximately 15 percent[4]) use the "cold" polymerization process, which operates at 4°C (40°F). The degree of conversion of monomers to copolymer for the cold process is less than for the hot process, so recovery and recycle of unreacted monomers is used in cold process latex plants. Also, some crumb plants produce small amounts of latex as an end product using the cold polymerization process. The discussion that follows is for the more predominant hot process.

Completion of the polymerization process requires from 6 to 24 hours. The latex is sent to a blowdown tank where, under an absolute pressure of 6.5 kPa (28 in. of mercury vacuum) and steam agitation, any unreacted butadiene and some unreacted styrene are removed from the latex. The overhead stream from the blowdown tank is sent to a water-cooled condenser where any condensibles are removed from the vapor stream and sent to a wastewater treatment facility. Noncondensibles from the condenser are discharged to the atmosphere.

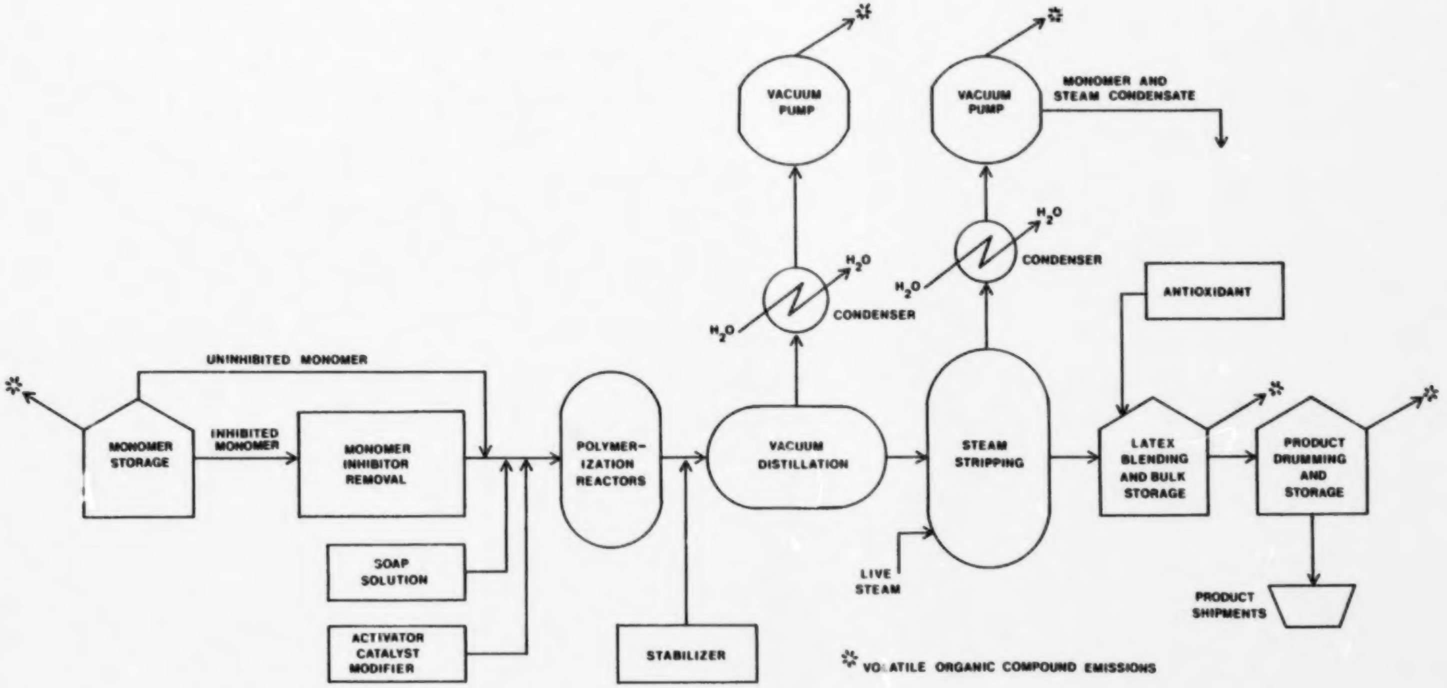
UNINHIBITED MONOMER
MONOMER STORAGE
INHIBITED MONOMER
MONOMER INHIBITOR REMOVAL
SOAP SOLUTION
ACTIVATOR CATALYST MODIFIER
POLYMER-IZATION REACTORS
STABILIZER
VACUUM DISTILLATION
H_2O
H_2O
CONDENSER
VACUUM PUMP
STEAM STRIPPING
LIVE STEAM
H_2O
H_2O
CONDENSER
VACUUM PUMP
MONOMER AND STEAM CONDENSATE
ANTIOXIDANT
LATEX BLENDING AND BULK STORAGE
PRODUCT DRUMMING AND STORAGE
PRODUCT SHIPMENTS
VOLATILE ORGANIC COMPOUND EMISSIONS

Figure 19-1. Schematic flow diagram for latex production by emulsion polymerization.

After discharge from the blowdown tank the latex is stored in process tanks where additives are introduced based upon product specifications. Starting from this point in the manufacturing process to the final product storage for shipment, latex is processed on a continuous basis.

Subsequently, the latex is screened using shaker screens to remove any large, agglomerated solids present in the latex. If the unreacted styrene content of the latex has not been reduced sufficiently to meet product specifications in the blowdown step, the latex is introduced to a series of steam-stripping steps to reduce the unreacted styrene content. Any steam and styrene vapor from these stripping steps is taken overhead and sent to a water-cooled condenser. Any noncondensibles leaving the condenser are vented to the atmosphere. The liquid stream from the condenser is discharged to the wastewater treatment system.

The stripped latex is then passed through a series of screen filters to remove unwanted large solids and is stored in blending tanks where antioxidants are mixed with the latex. Finally, latex is pumped from the blending tanks to be packaged into drums or bulk loaded into railcars or tank trucks.

Emissions and Emission Sources

The operating parameters of a model latex plant are presented in Table 19-2. Based on source sampling data and industry supplied information, the VOC emissions from the model plant sources were developed.[5-10] These data represent the expected annual emissions from the model plant in the absence of any add-on air pollution control equipment. Process control devices which are routinely applied for reasons of material recovery or plant safety are assumed present in the model plant. The use of these control devices is reflected in the emissions listed in Table 19-2.

TABLE 19-2. EMULSION LATEX MODEL PLANT[a]

VOC sources	Emissions (Mg/yr)	Vent flow (scfm)	Concentration (ppm)
Monomer removal - butadiene (1)	224	175	37,000
Monomer removal - styrene (1)	4	30	2,000
Blend tanks (15)	3 total (0.2/tank)	275 total (18/tank)	150

[a] Capacity of model plant is 30,000 Mg/yr and production rate is 27,000 Mg/yr.

Table 19-2 also reflects the composition of the copolymer product and the degree of conversion of monomers to polymer. The model latex plant is based on the use of a hot polymerization process with a 98.5 percent conversion of monomers to polymer, and a weight ratio of 46 percent styrene and 54 percent butadiene. Emissions will vary greatly in this type of plant depending upon the percent conversion, because the unreacted butadiene is vented without any reduction due to recovery operations. Emissions will also vary for different ratios of styrene and butadiene. Latex operations with less butadiene and more styrene will have lower emission rates because butadiene is more easily volatilized than styrene. The following factor can be used to estimate total emissions from plants producing latexes with different butadiene contents and percent conversions:

$$\text{Emission factor} = \left(\frac{100}{\text{percent conversion}} - 1\right)(933\, X_b + 67)\ \frac{\text{g VOC}}{\text{kg net copolymer}}$$

where X_b = weight fraction of butadiene in net copolymer.

"Net copolymer" means the reacted monomer content of the latex. The percent conversion to be used in this expression should be the percent of butadiene only fed to the reactor which reacts to form part of the polymer mass.

Table 19-2 lists the three major VOC emission sources for the emulsion latex model plant. Emissions from monomer storage tanks and reactor vents are not quantified. The reactors are normally sealed using rupture discs, with venting to a flare occurring only under extreme upset conditions within the reactor.

Monomer removal produces two vent streams in the model latex plant. Vented emissions from the blowdown process step consist mainly of unreacted butadiene, though some unreacted styrene is also emitted during this step. Because this portion of the manufacturing process is a batch operation, the venting of emissions is intermittent. Emissions from this operation account for approximately 97 percent of the VOC emissions from the emulsion latex process.

After the blowdown step, the latex is stored in process tanks. Product additives may be added in these tanks. The tanks also serve as flow-regulating holding tanks, because the remaining process operations are run on a continuous basis. The latex then flows through shaker screens to remove any large agglomerated solids. These screens are open to the atmosphere, but emissions are estimated to be very small. Concentrations of 42 ppm butadiene and 44 ppm styrene have been measured above the screens, but the air flow rate could not be determined.[10]

If the residual styrene content of the latex is greater than product specifications, the latex is processed in steam-stripping columns. The overhead styrene and water vapor stream is condensed in water-cooled condensers, and the noncondensibles are vented to the atmosphere. Table 19-2 shows that this noncondensible stream carries approximately 1.7 percent of the latex plant's VOC emissions with it. The stripped latex is then held in blend tanks, where antioxidants may be added. Evaporative emissions from the vents on the blend tanks are estimated to contribute another 1.3 percent of the plant's VOC emissions. This small amount of VOC would be emitted from 15 tanks in the model plant. The natural ventilation rates and low mass of VOC produce a stream of only 150 ppm organics.

CONTROL TECHNOLOGY

This section describes the emission control techniques available for control of VOC emissions in the styrene-butadiene latex manufacturing industry. The air pollution control techniques discussed are condensation and thermal and catalytic incineration. The costs of controlling the model latex plant with a thermal incineration system are also presented.

Condensers

Vapor condensation involves the removal of sufficient heat to liquify one or more of the vapors contained in the exhaust stream. The most common type of condenser for this application is a surface condenser consisting of a shell and tube heat exchanger. A coolant liquid is passed through the tubes of the exchanger while the gas stream passes on the shell side.

The primary disadvantage of condensation is its limited efficiency. The emissions reduction rate of a condenser is a function of the inlet VOC vapor concentration, because the outlet concentration is fixed by the temperature, pressure, and specific organic compound present. For example, an air stream at 4°C (40°F) and standard atmospheric pressure must contain over 2,800 ppm styrene before any styrene condensation will occur. However, condensers make excellent control devices for saturated streams (e.g., reduction of a stream containing 90 percent styrene to 6,000 ppm equals a removal efficiency of 99.3 percent). Therefore, condensers are only applicable to streams with high VOC content.

Currently, condensers are in use as process devices in most domestic latex plants. These units are an integral part of the manufacturing process and are primarily used for styrene vapor recovery to maintain desirable process economics, rather than as air pollution control devices. These condensers still provide a major reduction in VOC emissions, because the recovered styrene would otherwise be released to the environment.

Incineration

Incineration is the oxidation (combustion) of organic vapors present in a process vent stream. The factors governing the completeness of this reaction are time, temperature, turbulence, and the type and concentration of vapor present. Combustion air must mix thoroughly with the vapor at sufficient temperatures, usually 760 to 871°C (1400 to 1600°F), and for a sufficient period of time (0.5 to 0.75 seconds) to complete the combustion reaction. Combustion of vapors resulting from latex production results in the formation of carbon dioxide, water, carbon monoxide, and particulate.

In most applications it is necessary to provide auxiliary fuel to increase the heat content of the gas stream such that an adequate combustion temperature is reached. When sufficient VOC is present in the gas stream the combustion reaction will be self-sustaining, requiring no auxiliary fuel.

Plant insurance and safety regulations require sufficient margins of safety to ensure that the VOC vapor concentration of the gas stream remains above or below the explosive range of that vapor. This can be accomplished by keeping the stream above the explosive range by ensuring that the quantity of oxygen introduced into the gas stream (either through process requirements or inadvertent air leakage) does not create an explosive mixture or by keeping the stream below the explosive range by diluting it with ambient air. Most insurance companies require that the gas stream remain below 25 percent of the lower explosive limit in the absence of continuous VOC monitors. Concentrations as high as 50 percent of the lower explosive limit are allowed if a continuous monitor and alarm system are included in the design.

Two types of incinerators are discussed in this section, thermal (direct flame) and catalytic.

Thermal or Direct Flame Incineration

The basic thermal incinerator consists of an insulated combustion chamber fed by the burner(s) for the vapor stream and auxiliary fuel (if necessary) and a combustion air source. The vapor-laden stream is transported by a process blower through a preheat burner to raise the stream to a temperature suitable for combustion in the combustion chamber. Based on available data, thermal incinerators can reduce VOC emissions by 98 percent, if the stream contains more than 1,000 ppm organics. For more dilute streams the reduction efficiency is governed by the fact that approximately 20 ppm is the minimum outlet concentration that can be reached.[11]

The main advantage of thermal incineration is that it can be applied to all streams. This can enhance the cost effectiveness of this option by having one large incinerator control all VOC streams. Another advantage of thermal incineration is that generated heat can be recovered using either recuperative heat exchangers or waste heat boilers. Recuperative heat exchangers preheat the incoming vapor stream to reduce the heat addition requirements for combustion. This method can reduce incinerator energy requirements by 30 to 70 percent.[12] Similarly, high temperature exhaust gas from the incinerator can be used to generate process steam using a waste heat boiler in cases where the generated steam can be used elsewhere in the latex manufacturing process.

One manufacturer has developed a thermal incineration system for the oxidation of dilute VOC emission streams.[13] The oxidation occurs by passing the exhaust stream through regenerative combustion beds. Thermal recovery efficiencies of 85 to 90 percent can be achieved by this system. The system utilizes a vertical cylindrical combustion chamber surrounded by a series of packed stoneware beds. The VOC exhaust stream is preheated in a hot stoneware bed and passes through the combustion chamber, which is kept at a temperature of 760°C (1400°F). The hot combustion gases pass through other stoneware beds, transferring the heat of combustion to these beds. Inlet and exhaust valves on each bed control the gas flow as the beds are depleted or saturated with heat. This heat recovery system can substantially decrease the amount of auxiliary fuel required by the thermal incinerator.

Potential disadvantages associated with the use of thermal incineration systems at latex plants include variations in the stream flow rate which can lead to either automatic shutdown from surges or repositioning of the flame zone in the exhaust gas entrance to the vapor control unit.[14] The flow rate problem can be minimized by proper equipment design, such as the installation of fast response temperature feedback controls for combustion air and auxiliary fuel flows to maintain constant combustion characteristics in the thermal incineration system.

Two styrene-butadiene latex manufacturers have attempted to use thermal incineration as a VOC emission control technique. One unit encountered problems in handling the surges of emissions from the batch process of butadiene removal. This unit is no longer operating. The second unit has been reducing emissions from the monomer removal vents for ten years. Test results have shown that this unit reduces emissions by 99 percent based on organic carbon. When properly designed, thermal incineration is considered a suitable technique for VOC emissions control in the latex industry.

Control cost estimates have been developed for the installation of thermal incineration systems with 50 percent and 70 percent recuperative heat recovery capabilities controlling the butadiene removal vent of the model plant detailed above. The total installed capital costs and the annualized costs for these systems are presented in Table 19-3. These incineration systems are sized for 12,000 scfm, in order to handle the surges of emissions from the butadiene removal vent and the dilution air that will be needed to keep the waste gas stream below 25 percent of the lower explosive limit. The average flow rate of 1300 scfm at 5000 ppm butadiene was used to determine electricity and natural gas requirements. Incineration temperature is 1600°F and retention time is 0.5 seconds. Table 19-3 shows that no natural gas is required in the system that recovers 70 percent of the flue gas heat. No natural gas would be required for the model parameters used here for heat recoveries of 55 percent or more. Any additional heat recovery would require diluting the waste gases even more, or utilizing the heat for steam generation or space heating. No recovery credits have been included for this heat utilization because it would be very site specific and would also require additional piping, controls, and heat exchangers.

TABLE 19-3. ANNUALIZED COSTS OF IMPLEMENTING RACT
(June 1980 dollars)

Cost item	50% heat recovery	70% heat recovery
Installed cost ($)		
Purchased equipment[a]	154,500	180,600
Total installed[a]	336,300	393,000
Annualized cost ($/yr)		
Annualized capital charges		
Capital recovery[b]	54,700	64,000
Taxes, insurance, and administration[c]	13,500	15,700
Subtotal	68,200	79,700
Direct costs		
Operating labor[d]	6,100	6,100
Maintenance labor[e]	6,000	6,000
Natural gas[f]	5,000	0
Electricity[g]	1,000	1,000
Subtotal	18,100	13,100
Recovery credits	--	--
Net annualized cost	86,300	92,800

[a] Reference 15.

[b] Capital recovery factor of 0.16275 is based on 10 year life and 10 percent interest rate.

[c] Total of 4 percent of total installed cost per year; 1 percent for taxes; 1 percent for insurance; 2 percent for administration.

[d] Based on $11.10 per hour.

[e] Based on $10.90 per hour.

[f] Based on $2.40 per 1000 SCF.

[g] Based on $0.0490 per Kw-hr.

Catalytic Incineration

Catalytic incineration is similar to thermal incineration in both principle and operation. The difference is that combustion is completed in a catalyst bed which reduces requirements for both temperature and residence time. The temperatures required for combustion range from 204 to 538°C (400 to 1000°F), with shorter residence times than thermal incineration.[12] The lower temperature and shorter residence time requirements can lower operating costs by as much as 30 percent compared to thermal incineration in some applications.[16]

The catalyst employed may consist of any of several compounds, deposited in thin layers on an inert substrate. The substrate is formed into specific geometric configurations designed to maximize surface area and structural integrity while simultaneously minimizing pressure drops and ensuring a uniform, evenly distributed air flow. The performance of the catalyst is dependent on the contact time and temperature, as well as the organic composition and concentration of the vapor stream.[17] Deactivation of the catalyst occurs periodically from sintering and accumulation of poisons. Although the accumulation of poisons is to some extent reversible, sintering will eventually deteriorate the catalyst, requiring its replacement. Catalyst lifetimes, in continuous use, usually range from about 1.5 to 2 years,[12] but lifetimes of up to 7 years have been reported.[17]

Catalytic incinerators have the advantages of smaller size and lower heat requirements compared to thermal incinerators with low heat recoveries. These factors decrease both the capital costs (smaller size and lower cost materials of construction due to lower temperatures) and operational costs for auxiliary fuels. Similar to thermal incinerators, both recuperative heat exchangers and waste heat boilers may be employed to further reduce operating costs.

The principle disadvantage of catalytic incinerators is the high cost of the noble metals used for catalysts, which require periodic replacement. In addition to poisoning and sintering, as described earlier, the deposition of polymeric material on the catalyst could occur, decreasing the catalyst efficiency or partially plugging the catalyst bed.

Although no manufacturer of latex has attempted to use catalytic incineration as an emissions control technique, this method is applicable to any dilute hydrocarbon stream without heavy metal poisons.[18] Catalytic incinerators should provide 90 percent removal efficiency of VOC vapors.[12]

REGULATORY STATUS

State regulations which would apply to the control of VOC emissions from styrene-butadiene latex manufacturing are summarized in Table 19-4. These regulations are not specific for this industry, but rather are the general regulations which apply to any VOC sources greater than a certain size, usually 100 tons or more of VOC per year.

TABLE 19-4. SUMMARY OF STATE VOC EMISSION REGULATIONS[a]

State	Summary of regulation
California	Pumps and compressors must have mechanical seals or equivalent. Pressure relief valves must be vented to a vapor recovery or disposal system, protected by a rupture disc, or maintained by an inspection system.
Connecticut	Pumps and compressors must have mechanical seals or equivalent. Waste gases must be burned by smokeless flare or equivalent.
Delaware	No applicable regulation.
Georgia	No applicable regulation.
Kentucky	No applicable regulation.
Louisiana	Pumps, compressors, and valves must be equipped with mechanical seals or equivalent. Waste gases must be burned at 1300°F for 0.3 seconds or more in a direct flame afterburner or equivalent.
Massachusetts	No applicable regulation.
Michigan	No applicable regulation.
Minnesota	No applicable regulation.
North Carolina	No applicable regulation.
Ohio	Liquid organics must be reduced by 85 percent before discharge to the atmosphere. Waste gases must be burned by smokeless flare or equivalent.
Pennsylvania	Gaseous emissions must be burned by smokeless flare.
Tennessee	No applicable regulation.
Texas	Vent gases must be burned at 1300°F in a smokeless flare or direct flame incinerator.

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[a] In addition to the regulations in this table, States may have "odor" and "nuisance" regulations that may be applicable to the control of VOC emissions from styrene-butadiene latex operations.

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